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The Franklin Institute
Devoted to Science and the Mechanic Arts

Vol. 216 JULY, 1933 No. 1

THE ATOMIC NUCLEUS AND HIGH VOLTAGES.*

BY

M. A. TUVE,

Physicist, Department of Terrestrial Magnetism of the Carnegie Institution of Washington, Washington, D. C.

Before launching into the description of the work which I shall have the pleasure of telling you about this evening, you may wish to understand the reason why a program of research in nuclear physics is being carried out in the Carnegie Institution's Department of Terrestrial Magnetism. The two subjects are not as unrelated as casual thought would make them seem, and the basis of the relation can be expressed most briefly in the statement that the Institution and the Department for many years have taken the far-seeing position that the problems of terrestrial magnetism will never reach a really satisfactory solution until we possess an adequate understanding of the basic phenomenon of magnetism itself. Many of you will recall the important work carried out by Dr. Barnett at the Department in determining the so-called gyro-magnetic ratio, bearing on the ratio of the charge to the mass of the carriers of electric current in a conductor. At the time he undertook these studies probably no more fundamental problem in magnetism could have been enunciated. In the intervening years a great deal has been learned about the electrical and magnetic properties of crystals, molecules, atoms, and atomic parts. The work I shall

* Presented at a meeting held Thursday, February 2, 1933.

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describe this evening is the present development of a program in nuclear physics begun in 1926 under the direction of Dr. Gregory Breit, who resigned in the fall of 1929 to join the faculty of New York University, but whose interest and counsel we are still fortunate to have in his capacity as a Research Associate of the Institution. Throughout my talk this evening I shall ask you to bear particularly in mind that this work is a group-activity in which I have been so fortunate as to have a modest part. Especially to be mentioned are my immediate colleagues, Messrs. L. R. Hafstad and O. Dahl, and the Acting Director of the Department, J. A. Fleming, without whose active interest and support the work could neither have been begun nor carried forward.

By 1926 it was clear that the most basic and informative difficulties in modern physics involved our knowledge—or rather, lack of knowledge—of the laws governing the interaction of the primary material particles at very close distances, exemplified by the fact that most of the primary particles in the universe are combined to form atomic nuclei, held together in a manner and by forces the exact laws of which we still know very little about. Magnetism, as indicated by the chart I shall present at the end of the lecture, has proved to be one of the most basic forces in nature, and is indeed one of the few properties possessed by the electrons and protons which are the building-blocks of the universe. A study of the interactions of these primary particles has thus become essential to a description and elucidation of the basic phenomenon of magnetism.

Turning to the subject-matter of the evening's discussion let me present a chart (Fig. 1) which will serve to orient us as to the position of the atomic nuclei with which we are concerned in the scale of sizes of things. Note that if we consider the whole range of known (measured) dimensions, from the distances to the farthest nebulæ visible in the 100-inch telescope on Mount Wilson to the diameters of the nuclei we are studying, the distance from Baltimore to Washington is approximately the half-way point (on the logarithmic scale of Fig. 1). To reach the average size of an atomic nucleus, you must divide this 40-mile distance by the same tremendous number as you must multiply it by to

reach the distance of 300,000,000 light-years. Atomic nuclei are thus very small indeed, and if we insist that in a consideration of the problems of nuclear physics you must leave behind some of your ordinary six-foot concepts of every-day life, this chart may serve as our excuse.

FIG. 1.

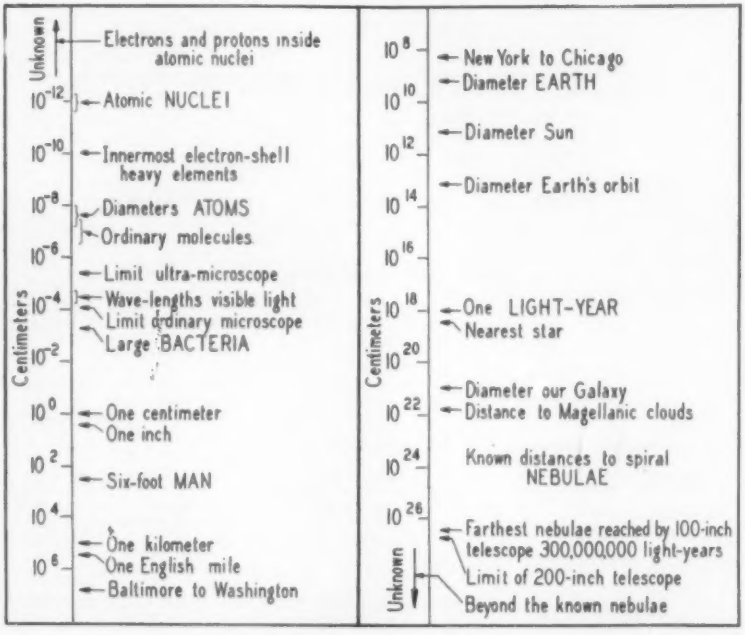
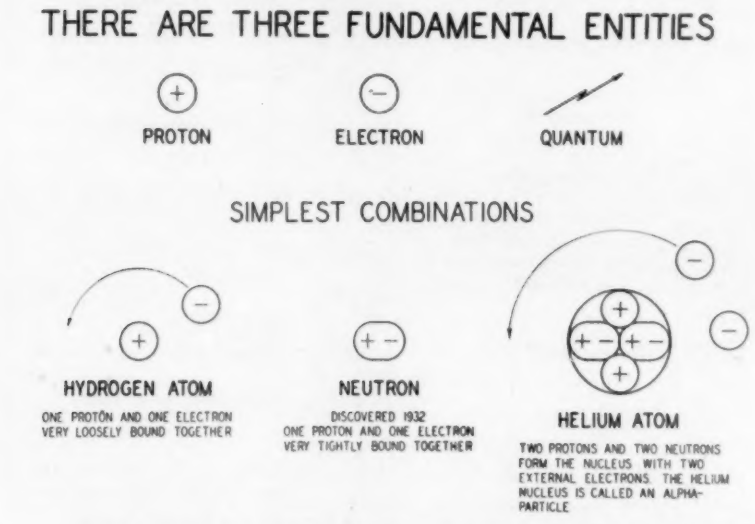


Chart of known dimensions.

I have spoken of the fundamental particles which are the building-blocks of the material universe. Figure 2 indicates that in addition to the electrons and protons (the proton, being much heavier than an electron, may possibly be still further divisible, but at all events it forms a very basic structure-unit in all atoms) we must consider energy in the form of light-quanta in any enumeration of basic building-blocks. This evening, however, we shall concern ourselves chiefly with the material particles which combine to form the atomic elements which we know as ordinary matter. Some of the simplest combinations of these primary particles are

also shown (Fig. 2)—the hydrogen atom, the neutron (which was discovered less than a year ago and is at present believed to be a very close combination of an electron and a proton, although this view is certainly tentative), and the helium atom. These schematic diagrams show the particles on a greatly distorted scale; for example, with the helium nucleus given the size it has in Fig. 2, the two outer electrons which

FIG. 2.


THERE ARE THREE FUNDAMENTAL ENTITIES
PROTON
ELECTRON
QUANTUM
SIMPLEST COMBINATIONS
HYDROGEN ATOM
ONE PROTON AND ONE ELECTRON VERY LOOSELY BOUND TOGETHER
NEUTRON
DISCOVERED 1932
ONE PROTON AND ONE ELECTRON VERY TIGHTLY BOUND TOGETHER
HELIUM ATOM
TWO PROTONS AND TWO NEUTRONS FORM THE NUCLEUS WITH TWO EXTERNAL ELECTRONS. THE HELIUM NUCLEUS IS CALLED AN ALPHA-PARTICLE
EVERY ATOM HAS A CENTRAL NUCLEUS, WHICH IS HEAVY AND POSITIVELY CHARGED, AND IS SURROUNDED BY ENOUGH NEGATIVE ELECTRONS TO MAKE THE ATOM ELECTRICALLY NEUTRAL.
THESE ATOMIC NUCLEI ARE BUILT UP OF PROTONS AND ELECTRONS, PARTLY BOUND TOGETHER IN SUB-UNITS, SUCH AS NEUTRONS.

The three fundamental entities—the proton, the electron, the quantum—and their simplest combinations.

make it a helium atom should be drawn at a distance of about one-quarter mile (20,000 times that shown). Even then the picture would only be schematic, as these outer electrons are not just charged spheres in fixed positions or orbits. For the rest of our discussion we shall omit consideration of the outer parts of the atoms—the electrons which balance the positive charges on their nuclei—and concern ourselves only with the atomic nuclei themselves.

Physicists are endeavoring to learn, then, how these basic structure-units are assembled in the formation of the nuclei of various kinds of atoms. The current stage of these efforts is indicated for the lightest elements, which are the simplest, in Fig. 3. Assuming that complex nuclei are built up of

FIG. 3.

THE STRUCTURE OF THE NUCLEUS OF AN ATOM DETERMINES ITS MASS AND ITS POSITIVE CHARGE, HENCE DETERMINES WHAT KIND OF A CHEMICAL ELEMENT IT FORMS

TENTATIVE TABLE OF ATOMIC NUCLEI

ATOMIC NUMBER	CHEMICAL ELEMENT	MASS	NUCLEAR STRUCTURE
1	HYDROGEN	1	1 PROTON
1	$HYDROGEN_2$	2	1 PROTON, 1 NEUTRON
2	HELIUM	4	2 PROTONS, 2 NEUTRONS } 1 ALPHA-PARTICLE
3	$LITHIUM_6$	6	3 PROTONS, 3 NEUTRONS } 1 ALPHA-PARTICLE, 1 PROTON, 1 NEUTRON
3	$LITHIUM_7$	7	3 PROTONS, 4 NEUTRONS } 1 ALPHA-PARTICLE, 1 PROTON, 2 NEUTRONS
4	BERYLLIUM	9	4 PROTONS, 5 NEUTRONS } 2 ALPHA-PARTICLES, 1 NEUTRON

THIS TABLE IS IN PROCESS OF BEING CONSTRUCTED AND ESTABLISHED

The sequence of chemical elements; tentative table of atomic nuclei.

simpler parts, in some such fashion as that shown, which following Heisenberg tentatively incorporates neutrons as subunits in the various nuclei, there are only certain questions which it is legitimate to ask concerning these structures. The familiar example of a question without a point "What color is an electron?" may indicate what I mean. In the nucleus it appears to be even more radically improper to carry over our ordinary concepts; for example, the present description of nuclear mechanics makes it an improper question to ask where an electron has been between-times if we know that at one time it is in a given position and at a

later time it is in approximately another position. There is even a relation, called Heisenberg's Uncertainty Principle, which states that if we know exactly where an electron is, we cannot know its velocity (momentum) within finite limits. There is a limit to the exactness within which we can know the product of the position and the momentum of a particle. The description of particle-position is restricted in this modern atomic mechanics to a statement of *probability*, as contrasted with our ordinary concepts of where things are and how they move. I only mention these points to indicate some of the limitations which are recognized as to the type of question it is possible to ask concerning the minute cosmos of atomic nuclei.

There are, however, certain questions which are quite pertinent and significant. We may inquire, for example, how many particles of each kind go into the formation of a given nucleus, and with what energies they are bound together. We may inquire what forces are experienced by a proton, for example, when it comes very close to one of these nuclei; whether it can sometimes even penetrate the nucleus and, if so, whether anything happens to the original configuration. There are two general methods at present by which we can learn the numbers of particles in different nuclei and their energies of binding. One method is that of very accurate determinations of the masses of the nuclei, as in the mass-spectrograph measurements by Aston, and now recently in the beautiful work of Dr. Bainbridge in the Franklin Institute's own Bartol Research Foundation Laboratory. The masses of different nuclei are found to be nearly integral multiples of a given unit, the integer representing the number of protons in the nucleus. The small departure from an exactly integral multiple (called the "mass-defect") gives a measure of the total energy of binding of a nucleus, since an amount of energy E has a mass $m = E/c^2$, where c is the velocity of light. The second method is the one we are using, namely, by bombarding nuclei of different types with high-speed protons and other atomic projectiles one can disrupt many of them into various component parts, and by studying such "reactions" one can draw conclusions as to the structures and energies involved. Studies of the scatter-

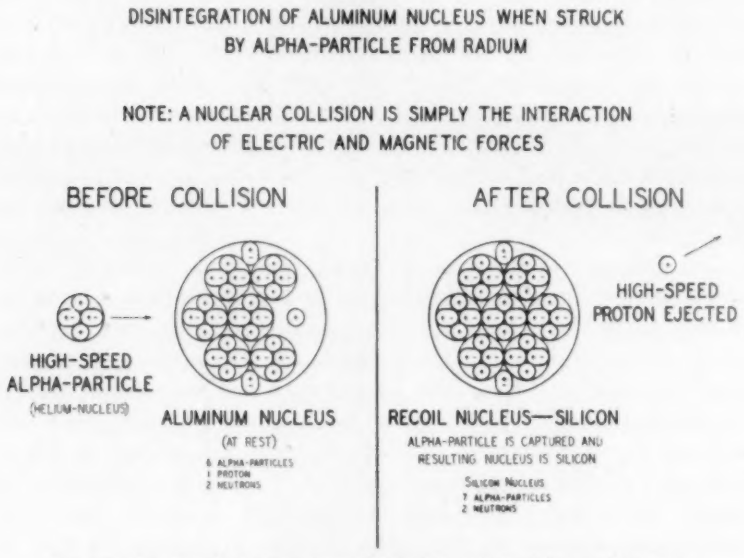
ing in various angles which is suffered by a beam of such projectiles also gives information as to the forces encountered in collisions with nuclei. Radium is a natural source of atomic projectiles of sufficiently high speed to approach closely and even penetrate various nuclei. The alpha-particles from radium have a positive charge of $2e$ ($-e$ = charge of one electron), and are ejected with a kinetic energy equal to that which such a charged particle would acquire in falling through a potential-difference of 3.6 million volts, that is, 7.2 million "electron-volts" energy. This at once indicates why high voltages are associated with atomic nuclei. Artificial, controllable, high-intensity sources of such high-speed particles may be obtained by the application of very high voltages to special vacuum-tubes which are provided with a source of low-speed particles, such as helium or hydrogen ions from an ordinary arc, at the positively charged end. Energies as high as several million electron-volts are desirable but not essential, especially if protons are used instead of helium ions as the projectiles.

An example of the type of "superchemical" reactions with which we are dealing is indicated in Fig. 4, which shows one of the ways in which an aluminium nucleus can be disintegrated. It is a reaction which we will consider in more detail presently. If a thin aluminium foil is bombarded by the alpha-particles (high-speed helium nuclei) spontaneously emitted by a quantity of radium, one in several hundred thousand of these particles collides, before it dissipates its energy in minor collisions, sufficiently head-on with an aluminium nucleus to penetrate it, and a certain fraction of those which penetrate will be captured. When this occurs, we observe a high-speed proton emitted from the aluminium foil, and by measuring its energy and knowing the energy of the original alpha-particle, we gain information as to the reaction which has occurred. These high-speed protons ejected from the aluminium nuclei may be observed by electrical counters, or may be actually seen in the Wilson cloud-chamber.

About two years ago the high-voltage part of our program had progressed to a point where we had produced and verified the several types of high-energy radiations useful in such

work, exactly similar to the radiations from radium, and we turned to the construction and development of the various instruments necessary for the detection and study of nuclear events. At the same time we undertook to carry out two or three problems of special importance using the older technique of radioactive sources. This was done for two reasons: To insure the correctness of the deductions we would make using the high-voltage technique, and because of the intrinsic importance of the radioactive experiments them-

FIG. 4.



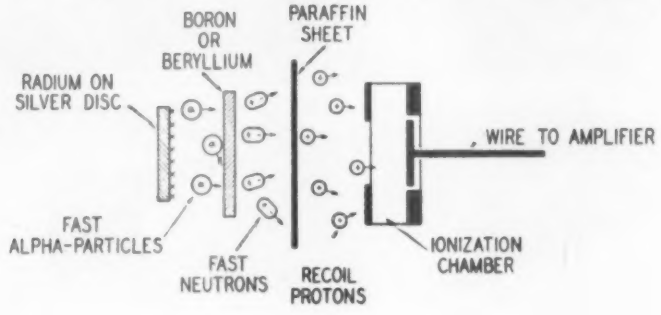
Interpretation of typical observations; disintegration of aluminium nucleus when struck by alpha-particle from radium.

selves. One of these experiments, on resonance-disintegration, I shall discuss presently, but first I shall describe some experiments we carried out last September on the new type of particle called the *neutron*, discovered last spring by Chadwick in Cambridge, who was led to make his experiments and conclusions by earlier results obtained by Bothe and Becker in Germany, and by Irène Curie and Joliot in France. By reason of their fundamental significance, we undertook to repeat the salient features of Chadwick's experiments, and we obtained results supporting the same conclusion.

The experiment itself is rather simple (Fig. 5). A radioactive source emits alpha-particles which bombard a target of boron or beryllium. An ionization-chamber connected to a sensitive amplifier (Fig. 6) is placed near this target, and a sheet of paraffin, cellophane, or other hydrogen-containing material is placed directly in front of it. The amplifier, connected to an oscillograph, shows a succession of "kicks," due to individual high-speed protons ejected from the paraffin.

FIG. 5.

DISINTEGRATION OF BORON OR BERYLLIUM NUCLEI WHEN STRUCK BY ALPHA-PARTICLES FROM RADIUM



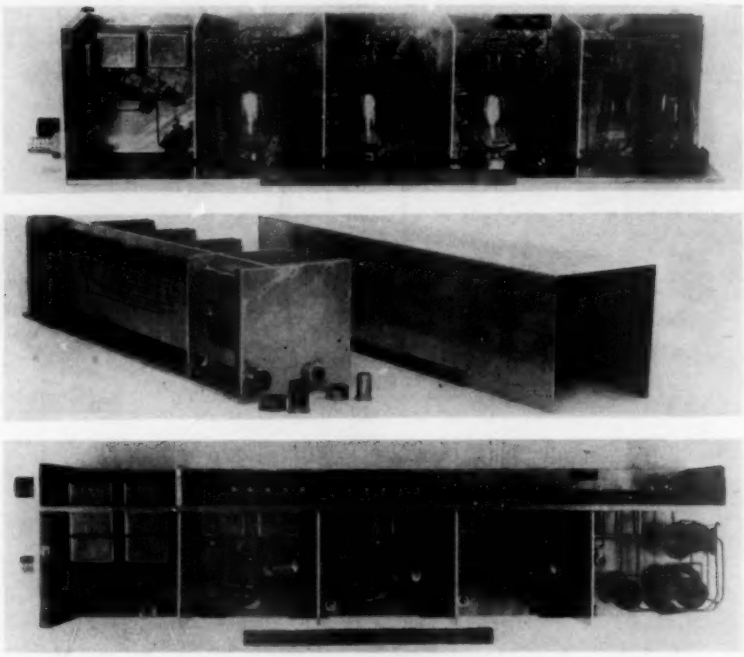
HIGH-SPEED PROTONS KNOCK ELECTRONS FROM ATOMS ALONG THEIR PATHS. ELECTRONS FREED IN THIS WAY INSIDE THE IONIZATION CHAMBER AFFECT THE FIRST TUBE OF THE AMPLIFIER, RESULTING IN A SHORT ELECTRICAL PULSE.

Production of fast neutrons; disintegration of boron or beryllium nuclei when struck by alpha-particles from radium.

In addition, a few larger kicks are present, which are due to recoil nitrogen-atoms in the ionization-chamber itself. If a lead plate is placed between the target and the paraffin sheet, the number of kicks is reduced surprisingly little, the absorption-coefficient corresponding to that of very hard gamma-rays. It was at first supposed that these radiations excited in boron and beryllium were indeed gamma-rays. Curie and Joliot calculated that if the high-speed protons, whose maximum energy is 5.7 million electron-volts, were produced by a recoil-process in which a high-energy photon (gamma-

ray) was scattered by a proton, as in the familiar Compton-effect process, when a photon is scattered by an electron, the photon from beryllium must have an energy of 50 million electron-volts. Chadwick repeated the experiment and checked this figure, and calculated that a nitrogen nucleus by the same process could acquire an energy of 450,000 electron-volts. He found experimentally, however, that nitrogen nuclei

FIG. 6.



Linear pulse-amplifier used for counting high-speed protons and alpha-particles.

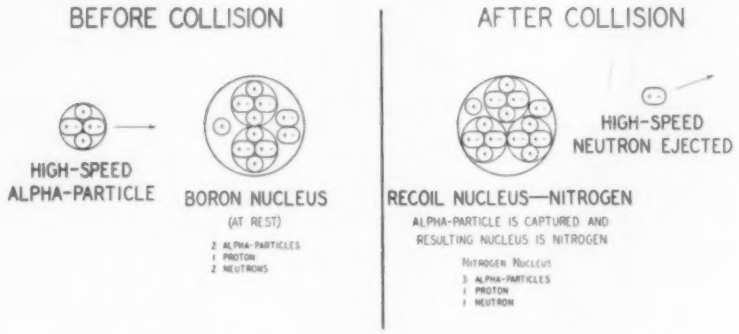
actually acquire an energy of about 1,200,000 electron-volts, which would require an initial gamma-ray photon from the beryllium having an energy of 90 million electron-volts! Since the primary radiation from the beryllium is the same for both cases, this is a very serious discrepancy, and by extending the measurements to other recoil-nuclei Chadwick showed that the idea of Compton-recoil encounters was

almost untenable. However, Chadwick pointed out that all of the data could be explained if one assumed the primary radiation from the beryllium (or boron) to be a stream of high-speed particles of mass 1 (mass of the proton) and with zero electric charge, their kinetic energy being 5.7 million electron-volts. Such particles could be expected to pass through the lead absorbers with little interference (because of their zero-charge) and the energies they would give to various recoil-nuclei, on the assumption of simple billiard-ball collisions, were exactly the energies measured experimentally. The nuclear reaction which is thought to occur is indicated

FIG. 7.

DISINTEGRATION OF BORON NUCLEUS WHEN STRUCK BY ALPHA-PARTICLE FROM RADIUM

NOTE: A NUCLEAR COLLISION IS SIMPLY THE INTERACTION OF ELECTRIC AND MAGNETIC FORCES



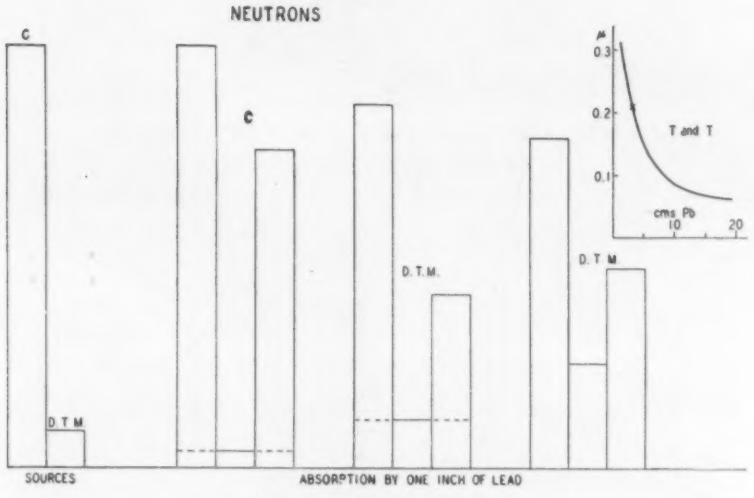
Interpretation of typical experiment; disintegration of boron nucleus when struck by alpha-particles from radium.

for boron in Fig. 7. From data as to the mass-defects of the nuclei involved in this reaction, Chadwick found the mass of the neutron to be 1.055 ± 0.008. This was the discovery of the neutron, which I might point out is simply the name and the picture which has been given to a certain set of experiments, very limited to date, which disagrees very definitely with our earlier data of experience. Confidence in the correctness of the name and the picture—which is at present very

satisfactory, especially because it removes many difficulties in our earlier views of the structure of nuclei—can only be slowly acquired as more and different experiments are carried out and found to support it.

In our laboratory we repeated the measurements of the maximum recoil-energies acquired by protons and by nitrogen nuclei, using the linear amplifier (Fig. 6) and the FP–54 pliotron (Fig. 12). In both cases we obtained values within a few per cent. of those observed by Chadwick. We also took several thousand stereoscopic photographs with the Wilson

FIG. 8.



Data on absorption of neutrons.

cloud-chamber (Fig. 9), observing and identifying the recoil nitrogen-nuclei. No attempt was made to assign disintegration-phenomena to neutron-collisions, as reported by Feather from Cambridge, who used Chadwick's strong neutron-source, because of the weakness of our polonium-source compared with Chadwick's (Fig. 8), and the uncertainty introduced by ever-present radioactive contamination in the air and in the walls of the chamber. In one respect, not affecting the conclusion that neutrons are actually present, our observations did not agree with Chadwick's. He found the neutrons from

beryllium to be absorbed only 13 per cent. by one inch of lead, based on counts of recoil nitrogen-nuclei. Counting recoil-protons, which presumably should give the same result, we found the neutrons from beryllium absorbed about 55 per cent. by one inch of lead, in two very brief series of observations. Figure 8 shows the recoil-counts with and without one inch of lead, with the residual counts (contamination) in between. The data from our measurements, however, agree at the point indicated in Fig. 8 with the absorption-curve for beryllium neutrons published by Thibaud and La Tour in October.

There are two general methods of chief importance for the detection and study of nuclear occurrences. Both methods depend on the fact that a fast-moving electrically-charged atomic fragment—a proton, electron or nucleus, but not a neutron—knocks electrons free from the outer parts of atoms with which it collides. This process, giving rise to numerous free positively and negatively charged "ions" along the path of the high-speed particle, is called "ionization." These free electric charges can be detected electrically in a number of ways, forming one general method of study. The ionization per centimeter of path produced by a fast-moving nucleus depends on its speed and on its charge, and even for a one-million-volt proton (charge = 1) it is of the order of 1500 ions; a helium nucleus (alpha-particle—charge = 2) of the same speed (not the same energy) produces four times this ionization per centimeter of path. Such a number of ions constitutes a readily detectable amount of electricity. During recent years a special type of amplifier, using radio tubes, has been found the most reliable method of identifying and counting such high-speed nuclei, by sweeping the ions produced in a measured length of path, corresponding to the depth of the ionization-chamber of Fig. 5, onto the grid of the input-tube of the amplifier.

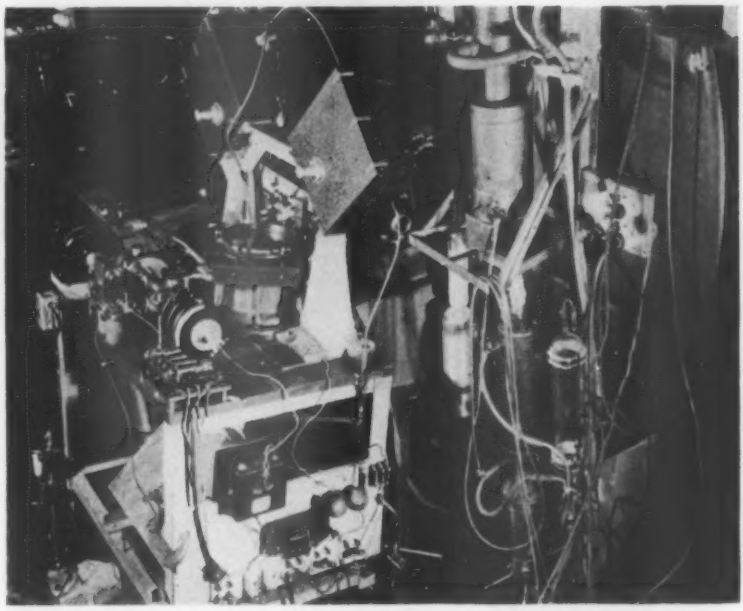
Those who are technically interested in amplifiers and circuits will be interested in some of the characteristics of the "pulse-amplifier" of Fig. 6, which is based on the design used in Cambridge. The simple shielding shown is ample, even for voltage-amplifications as high as 2,000,000, using "filter"-resistors and capacitors on all leads, immediately adjacent to

each tube. A Marconi DEV-tube was found the best of those available for the input-tube (floating grid) and a low-noise tube (PJ–11) is used in the second stage. A variable-μ tube (234) next to the output-pentodes gives a logarithmic or square-root-law response, of great convenience when using 35-mm. film for recording. Of chief interest and importance is the amplifier noise-level, which limits the smallness of the impulses which can be detected. With this amplifier a one-megohm resistance connected from the input-grid to ground increases the noise-level by a factor of six, due to the thermal agitation of the electrons in the one-megohm resistance (Johnson effect). It appears from our studies that no tube as yet available has ideal properties for use as the input-tube of an amplifier of this type, although with the present amplifier alpha-particles with a path-length of one-half mm. and very high-speed protons with a path-length of 15 mm. can always be detected. When supported on screen-door springs covered with rubber tubing, this amplifier works with remarkably low noise-level, allowing the detection of even very-fast protons in spite of the mechanical noise and electrical disturbance of the high-voltage generator which will be shown later.

The second general method of detecting and studying high-speed atomic fragments actually makes their paths visible to the eye as "fog-tracks," and was invented by C. T. R. Wilson of Cambridge in 1912. This method makes use of the fact that supersaturated water-vapor tends to condense readily on electrically charged particles. A closed chamber containing air and water-vapor is suddenly expanded by moving a piston, cooling the gas and causing a high degree of supersaturation. If a high-speed charged particle produces ions along a path in the gas, the water condenses on each of the ions, and this path is outlined in visible droplets of water. This technique is one of the most fruitful in studies of nuclear collision-phenomena. An automatic cloud-chamber apparatus for obtaining photographs of the tracks of high-speed protons from a high-voltage tube fed by a spark-excited Tesla coil (inside the oil-tank) is shown in Fig. 9. The two cameras give stereoscopic photographs of the fog-tracks produced in the round piston-chamber beneath them. A sample photograph with this arrangement, showing the tracks of

individual protons, one of which suffers a sudden deflection due to a nuclear collision near the end of its path, is shown in Fig. 10. This technique of the Wilson cloud-chamber has numerous applications, among them the study of the tracks of the penetrating-radiation, familiarly known in this country as "cosmic rays." A cloud-chamber which is permanently sealed and can be oriented in any direction is shown in Fig. 11. This instrument, utilizing a flexible metallic bellows or

FIG. 9.



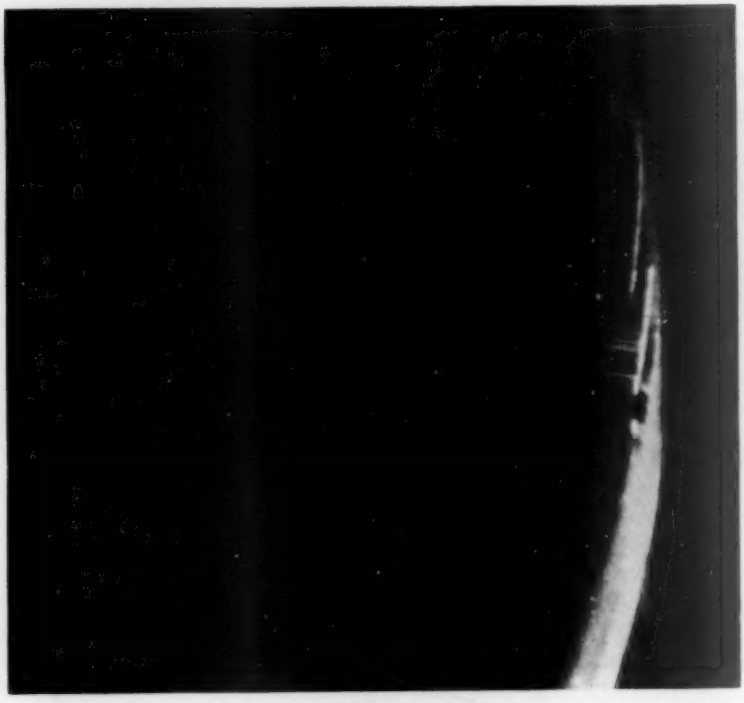
Automatic Wilson cloud-chamber used for photographing tracks of high-speed protons from high-voltage tube (in oil-tank).

"sylphon" has numerous advantages over the more usual piston-type cloud-chamber. Special mercury spark-lamps which give sufficient illumination to allow the use of positive cinema-emulsion of high resolving power also have been developed.

Another instrument to which we have given particular attention in the past two years, particularly by reason of its great promise in the measurement of extremely small amounts

of charge, or small electric currents, which are of great importance in nuclear physics studies and in many other fields of research, is the FP–54 pliotron. This tube is comparable in sensitivity to the best electrometer, and has certain advantages of convenience in use. My colleague, Mr. Hafstad, has explored the possibilities of this device rather completely,

FIG. 10.



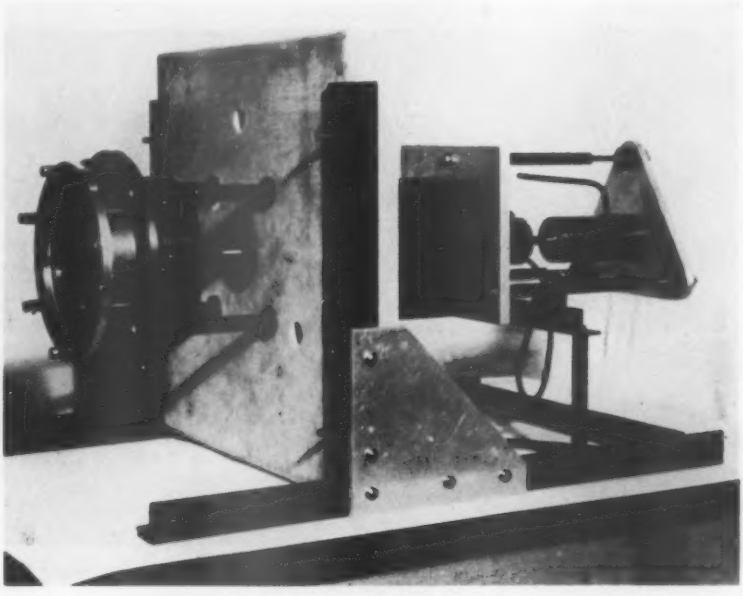
Tracks of single high-speed protons from a high-voltage tube. Note the sudden deflection of one track by collision of the proton with a nitrogen nucleus.

and because the measurement of minute quantities of electricity is fundamental in so many fields of research I will describe briefly the results of his tests.

The FP–54 pliotron has an input- (grid-) capacity of about 3 $\mu\mu$f and with an ordinary type R galvanometer gives a voltage-sensitivity of 250,000 mm. per volt with ease in a single-tube circuit. This is a charge-sensitivity of 80 electrons

per millimeter, an intrinsic sensitivity obviously beyond that of any mechanical electrometer. The most sensitive of the latter, the Hoffmann duant electrometer, attains a sensitivity of 2000 e./mm. with difficulty. However, the limits of *useful* sensitivity are set by fluctuations, and in the FP–54 the Schottky effect (fluctuations due to variations in the number of electrons arriving at the grid per unit of time) and the Johnson effect (fluctuations in grid-potential due to the

FIG. 11.

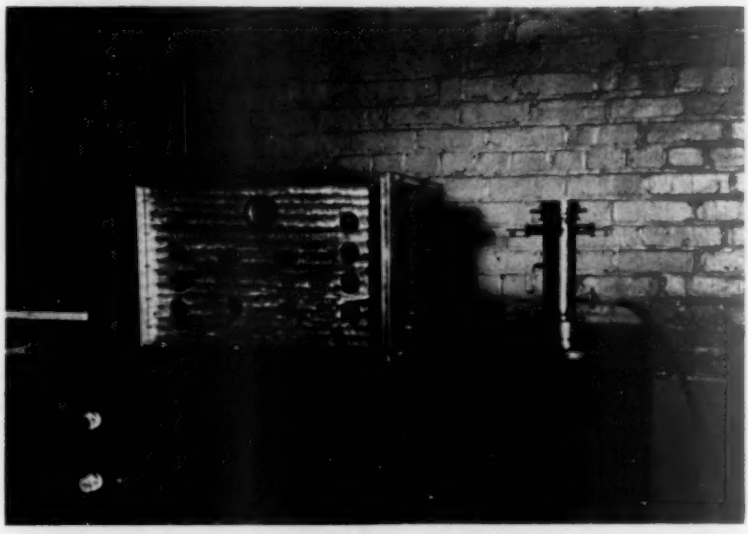


Sylphon-type Wilson cloud-chamber.

thermal agitation of the electrons in the supporting structures or resistors connected to it) are both present. Mr. Hafstad finds that a single FP–54 mounted in a vacuum (Fig. 12) actually attains the theoretical limit of sensitivity set by these fluctuations (± 640 electrons R.M.S. value), which are of the same order from both causes. He has actually used this instrument to measure a current of 7×10^{-18} ampere (45 electrons per second) to an accuracy of five per cent. in

a period of a few minutes (Fig. 13). The Hoffmann electrometer is limited in a similar way by thermal agitation—Brownian movement of the suspension or Johnson effect in the insulators, since the latter turns out to be independent of resistance for large values of *RC*. The limiting fluctuations for this instrument from published data are found to be about ± 1000 electrons. The FP–54 is thus well adapted to nuclear disintegration-studies involving the electrical detection of individual high-speed particles, for example, the disintegra-

FIG. 12.



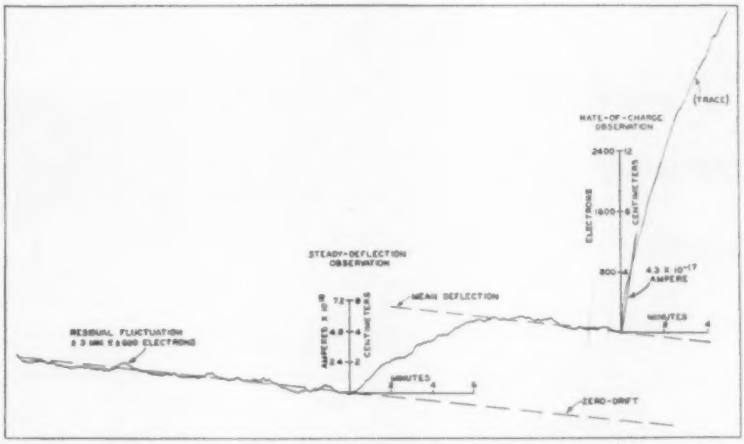
Set-up of single FP–54 pliotron used for measurement of very small currents and amounts of electric charge.

tion-protons from aluminium, which produce from 1500 to 10,000 ions per centimeter of path in air. It was in fact for this purpose that this FP–54 technique was developed in our laboratory.

Present-day atomic theory, called "wave-mechanics," pictures the alpha-particles and protons in a nucleus as "matter-waves" reflected back and forth between the potential "barriers" which determine the outer boundaries of the nucleus, and the disintegration of the unstable radioactive

nuclei is then a "leakage" of the matter-waves through the barrier, at a rate which determines (or is determined by) the average lifetime of the given type of nucleus. The probability of leakage through the barrier is greater for particles inside the nucleus whose energy is nearly equal to the height of the barrier (Fig. 14). Similarly the probability that a particle directly approaching a nucleus from the outside will penetrate the barrier and enter is very much increased as the energy of the particle is increased, and this

FIG. 13.

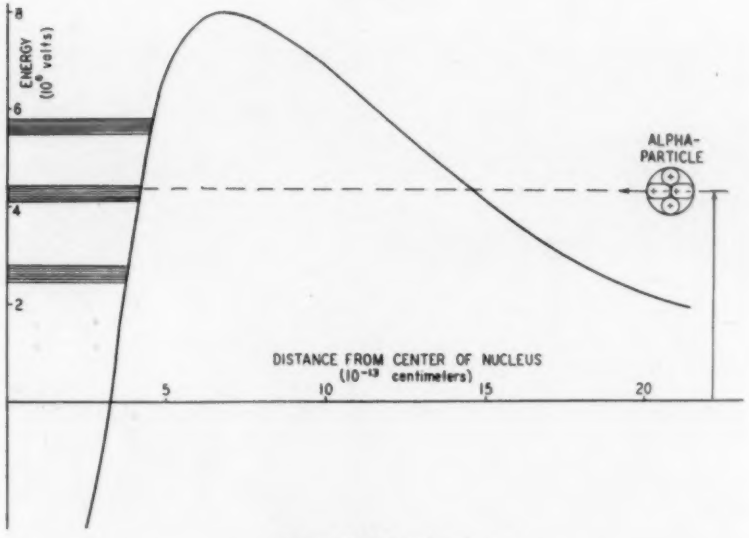


Example of very small current-measurement using single FP-54 pliotron.

probability is unity for particles whose energy exceeds the height of the barrier. In one particular respect the wave-mechanics differs vastly from the older classical picture. If "energy-levels" exist inside the nucleus, the probability that an approaching particle will penetrate the barrier is also very nearly unity if its energy of approach corresponds to the height of one of the nuclear energy-levels, due to a resonance-effect, natural enough on a "wave"-basis but totally foreign to the older point-charge picture of atomic and nuclear construction. Thus, if such a resonance-effect exists, an aluminium target, for example, could be almost unaffected by bombardment with alpha-particles of a given energy, but might be copiously disintegrated by alpha-particles of a

lower energy which happened to coincide with an energy-level of the aluminium nucleus. Observations which appeared to show this effect, called resonance-disintegration, were first made by Pose in Germany in 1930. Since then, Chadwick and others at Cambridge have sought this effect, first finding no evidence for resonance and then finding strong resonance-groups whose energy-values can hardly be said to agree with Pose's. Steudel, working in Meitner's laboratory in Berlin,

FIG. 14.

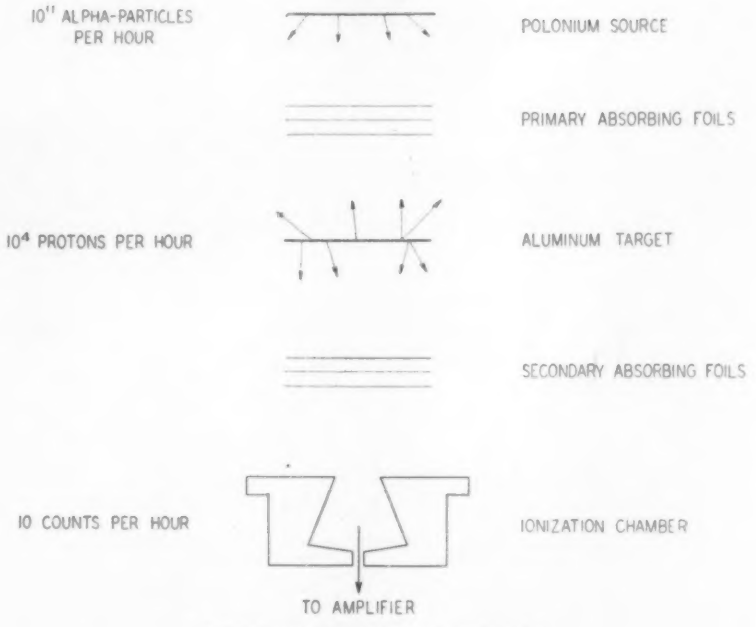


Potential barrier of nucleus.

has published data represented as strong evidence against the existence of resonance-disintegration. Leprince-Ringuet in Paris also failed to find evidence for resonance, and yet Diebner, working with Pose, has verified and extended the latter's beautiful and exhaustive experimental results in a recent paper. The arrangement of the source, target, absorption-foils, and detecting device is indicated in Fig. 15. The experiment consists in measuring the number and range (using the secondary absorbing foils) of the disintegration-protons (Fig. 4) emitted by the aluminium target as the range of the primary alpha-particles is *decreased* by means of the primary

absorption-foils. With a given range of alpha-particles striking the target, the protons arising from a resonance-process involving one nuclear alpha-particle energy-level should all have the same energy, giving rise to a "group" of protons of a given range. The existence of such groups is shown clearly in the data of Pose and Diebner in Fig. 16, which also gives some of the data of workers who failed to find evidence for resonance.

FIG. 15.

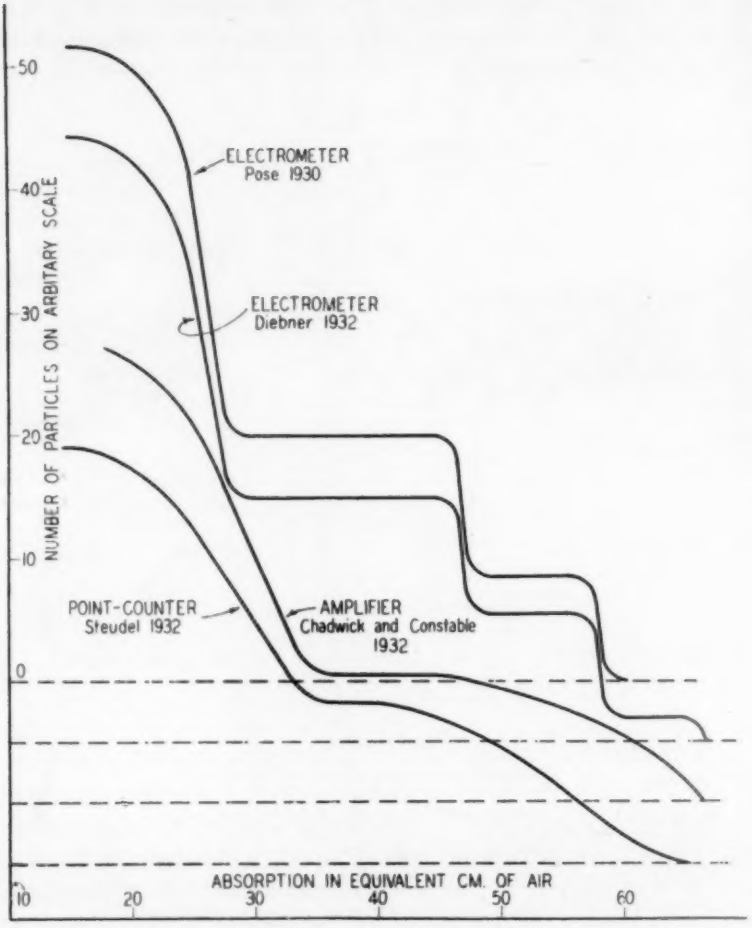


Resonance-disintegration by alpha-particles.

The FP–54 appeared to offer a new possibility of attacking this important question, and Mr. Hafstad has carried to partial completion a series of observations on aluminium, similar to Pose's, but using the FP–54 instead of the Hoffmann duant electrometer. Very strong evidence for the existence of resonance, with energy-levels similar to those found by Pose, exists in his data. In particular, the yield of disintegration-protons for 10^8 alpha-particles on the basis of an absolute calculation (dimensions, geometry, etc.) which he

obtains checks Pose's high value, in direct contradiction to Steudel's results. Furthermore, a consideration of the geometry of Steudel's apparatus shows that the resonance-

FIG. 16.

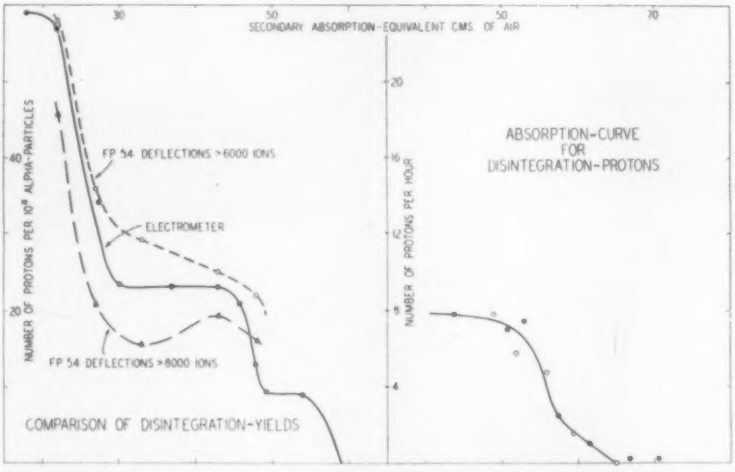


Absorption-curves for disintegration-protons.

groups would be wholly obliterated in his curves by the "washing-out" effect of the wide range of angles he uses. Hafstad also finds evidence for the sharp drops characteristic

of Pose's curves, at about 30 and 60 cm proton-range, although a mechanical accident to the apparatus interrupted his work, breaking the observations into two groups (Fig. 17) and necessitating a new polonium-source, now in preparation, for the careful investigation of the sharpness of resonance and the exact ranges of the groups. Since Fig. 17 represents the data from continuous records over a period of nearly eight months, some time will elapse before these questions can be studied completely.

FIG. 17.

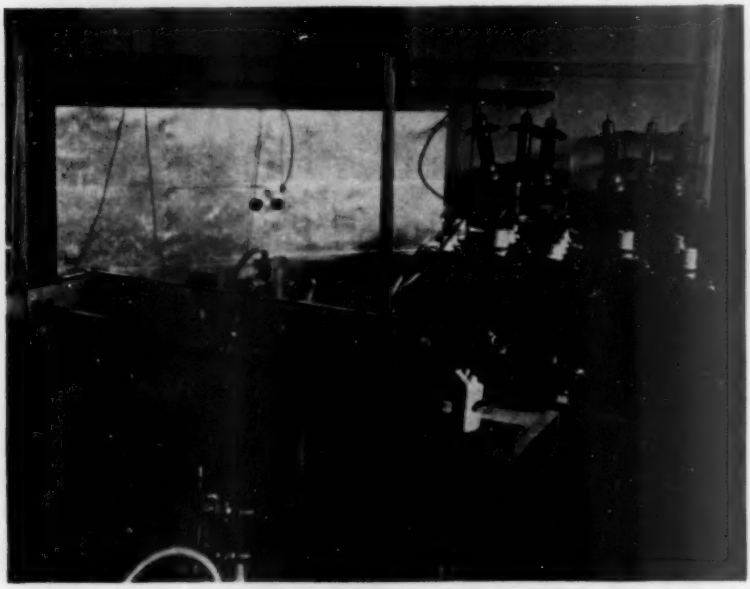


Results on the resonance-disintegration of aluminum using the FP-54 pliotron.

I shall now turn to the high-voltage phase of our work. When we started these investigations in 1926, the Tesla coil was adopted for study, because it constituted an inexpensive high-voltage source whose possibilities were largely unknown. The original installation, in a large wooden tank, is shown in Fig. 18. A method was devised for measuring the voltages produced, which were found to reach 3,000,000 volts. Using oil under pressure to increase its breakdown-strength, potentials exceeding 5,000,000 volts were attained. After investigating the limitation at 400 to 500 kilovolts existing with single-section vacuum-tubes, which was found to be related to the glass walls of the tube rather than to the degree of evacuation or the nature of the electrodes, tubes were designed

and constructed on the Coolidge cascade-principle, which operated successfully and without failure at voltages up to 1900 kilovolts. In spite of the limitations arising from the short on-time of the high voltage from the spark-excited Tesla coil, amounting at best to a few micro-seconds per primary spark, and the fluctuating nature of this voltage, the Tesla coils and cascade-tubes were used (1930–31) to produce high-speed electrons (beta-rays), hard X-rays

FIG. 18.

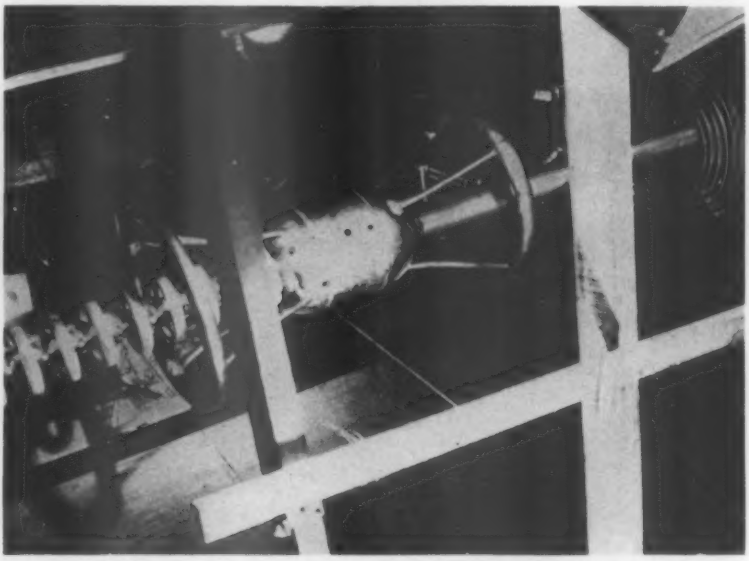


Original spark-excited Tesla-coil equipment which reached 3,000,000 volts.

(gamma-rays), and high-speed protons of energies above one million volts. Magnetic deflection-measurements verified the voltage-measurements made by the capacity-potentiometer-method, and a Thomson parabola-apparatus demonstrated unambiguously the high-speed protons. Photographs of proton-tracks were obtained in the Wilson cloud-chamber apparatus as shown in Fig. 9, and the range of 1100-kilovolt protons was found to be 29 mm., in air, indicating that these particles follow nearly the velocity-cubed law, which gives

the range of alpha-particles, rather than the v^4 law which applies for the faster beta-particles. A photograph showing the Tesla coil and cascade-tube in position on the large oil-tank used in these experiments is shown in Fig. 19. Note the "ring-shields" made necessary by the electrical transients of very steep wave-front which were encountered in this work.

FIG. 19.

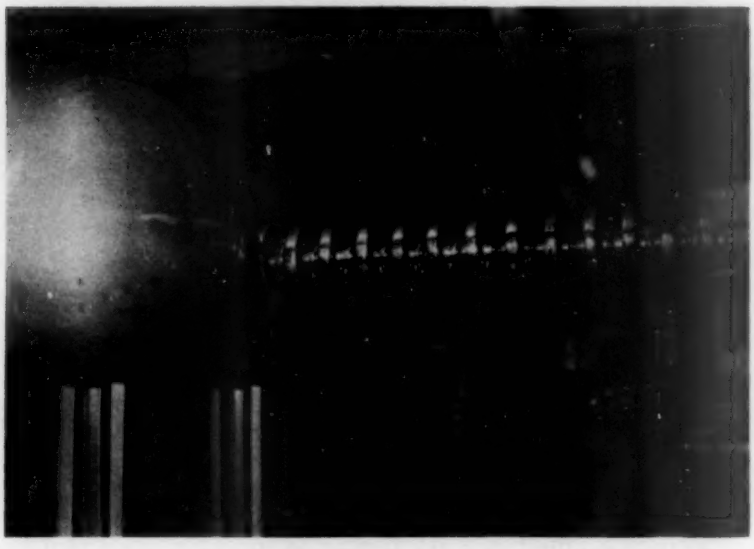


Tesla coil and cascade-type high-voltage tube in position in oil-tank.

By the summer of 1931 the provision of a more suitable voltage-source than the spark-excited Tesla coil became clearly imperative. This source has ample power-output (approximately one kw), but the very short on-time necessitates a proton-source of enormous instantaneous intensity, and then more fundamental difficulties arise in the interpretation of results with its use, because of the difficulty in counting the exact numbers of atomic events occurring in 10^{-6} second. Most methods and instruments used in such work, as above described, are limited as to time-resolution. We investigated the various possibilities available for a laboratory with limited funds, and were particularly impressed by the simple electro-

static generator devised by Dr. R. J. Van de Graaff, then a National Research Fellow at Princeton University. This generator is perhaps the simplest conceivable device for producing steady high potentials. It comprises a high-potential electrode of low curvature to reduce corona-losses, usually more or less spherical, and an insulating belt carrying electric charge to the electrode much in the manner of an ordinary bucket-hoist. We were in close touch with Dr. Van de Graaff's work, and when he had constructed two small

FIG. 20.

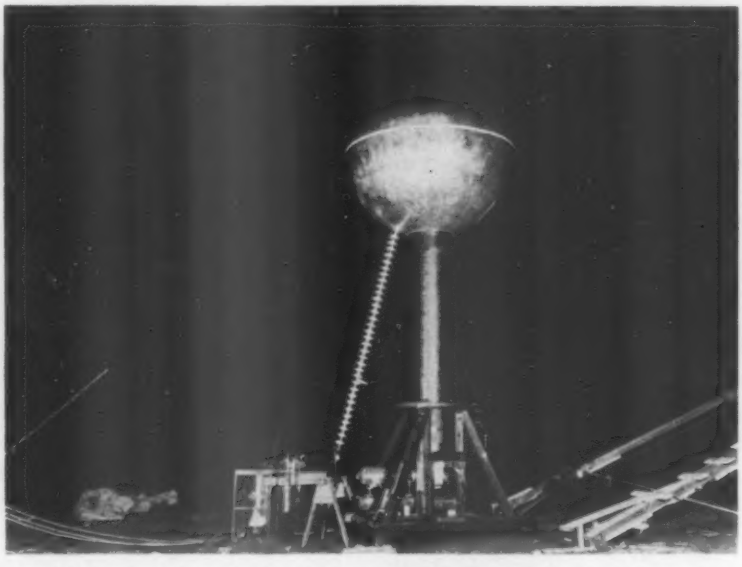


Coöperative tests of the original Van de Graaff generators on high-voltage tubes at the Department of Terrestrial Magnetism.

generators of this type for use in air a coöperative test was arranged whereby Dr. Van de Graaff's generators were brought to our laboratory in Washington for test on our high-voltage cascade-type tubes. A photograph showing these tests is shown in Figure 20. These tests at once showed that there was no new difficulty involved in the application of steady (direct-current) potentials to vacuum-tubes, a point hitherto not tested as all very high-voltage tubes up to that time had been used with fluctuating or alternating potentials.

In fact, we found considerably less difficulty in applying this steady potential than the Tesla voltages to our tubes, a fact amply confirmed by later tests. We then undertook the construction and test of a much larger generator of this type. Van de Graaff's original generators utilized 2-foot spheres, and we built one using a 2-meter sphere ($6\frac{2}{3}$ feet) to verify that the attainable voltage was proportional to the diameter of the sphere and to provide a voltage-source for the interesting region well above 1,000,000 volts. This generator was tested outdoors (Fig. 21) and voltages as high as 2,000,000

FIG. 21.



Out-door tests of the 2-meter Van de Graaff generator constructed by the Department of Terrestrial Magnetism.

volts were attained; the theoretical limit (30,000 volts per centimeter at the surface of the sphere) is about $3\frac{1}{3}$ million volts for a sphere of this size. The tube shown in Fig. 21 was too short to stand the full voltage, but reached about 1,000,000 volts with no difficulty within three hours after setting up the apparatus. Obvious difficulties prevented serious work with this equipment outdoors, and since the

necessary housing for this machine (now being provided) was not available, a smaller one-meter generator, adapted to the dimensions of our laboratory, was constructed.

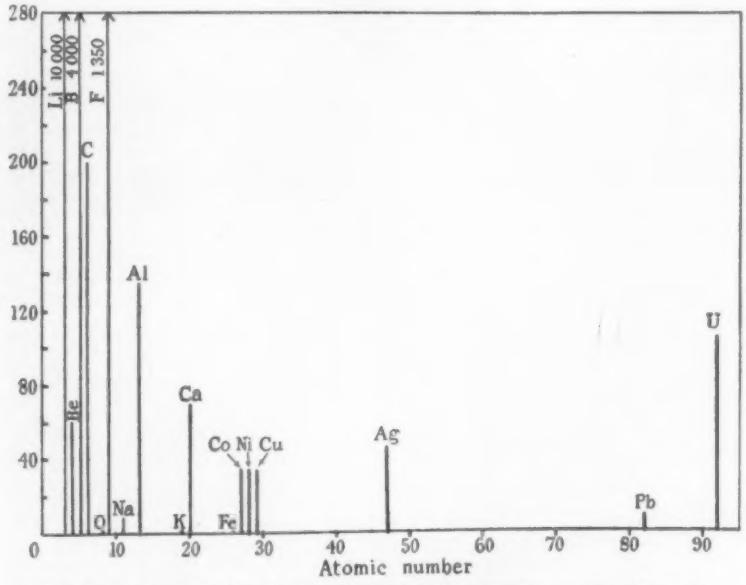
About the time of our tests of the larger generator, however, two young men in Lord Rutherford's laboratory in Cambridge, Drs. J. D. Cockcroft and E. T. S. Walton, achieved the first results in the high-voltage nuclear-physics program which was and is the goal of a group of laboratories in addition to our own.

Using a combination of condensers and rectifiers to multiply the voltage of a 200-kilovolt transformer to a direct-current potential of 700 kilovolts, and with a two-section vacuum-tube of the Coolidge cascade-type, they bombarded targets of various elements with a mixture of protons and hydrogen ions of energies up to about 600 kilovolts. They made the discovery that protons of energy as low as 125 kilovolts produced disintegrations of lithium nuclei, the Li_7-nucleus capturing a proton and forming two He_4-nuclei, which shared the 17,000,000 electron-volts energy known to be available in such a reaction and appeared as 8,500,000-volt alpha-particles. They also found that boron nuclei were readily disintegrated. By far the most striking feature of their results, however, and a feature which is distinctly disconcerting from the standpoint of all present-day theoretical ideas of the nucleus, is the fact that they also found a variety of heavier elements to be disintegrated by these quite moderate-energy protons. Figure 22, which is Fig. 7 of Cockcroft and Walton's paper, shows the numbers of disintegration-particles observed per minute per microampere with the particular geometry of their apparatus and for a potential of 300 kv. on their tube. These are scintillation-count measures, but they were checked for several elements and found to be alpha-particles by an amplifier of the type I have already described to you, and the fact that almost no counts were obtained for several elements strongly supports the reality of the counts obtained with the others. Even though Cockcroft and Walton present these figures as orders of magnitude only, the fact that they evidently find the heavier nuclei to be disintegrated in measurable numbers is almost beyond question the most important difficulty at

present involved in our understanding of the nucleus, and can fairly be said to have thrown nuclear theory into serious confusion. The magnitude of the discrepancy I hope to indicate briefly in a few moments.

Cockcroft and Walton's observations on the disintegration of lithium were promptly checked in this country last summer by Professor E. O. Lawrence and his colleagues at the University of California. They used an ingenious "proton-whirlpool" device for accelerating the protons, which are

FIG. 22.

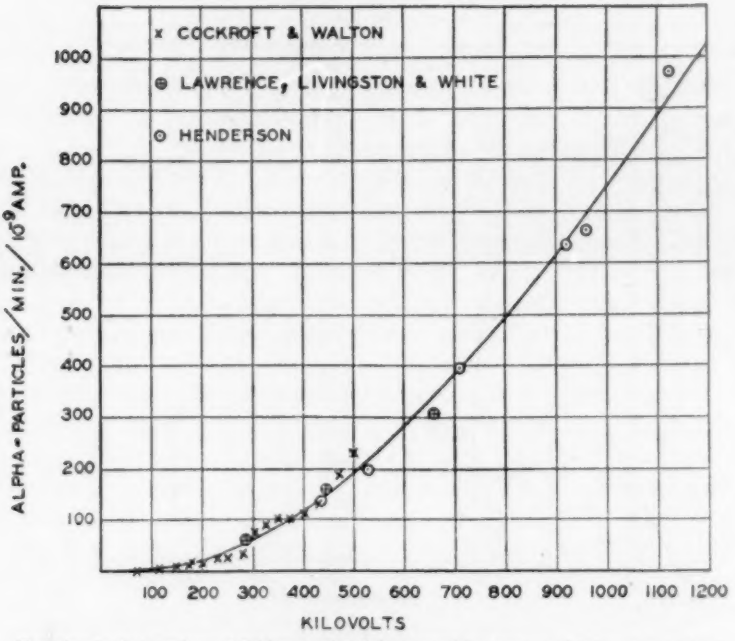


Relative numbers of nuclei of various elements disintegrated by 300-kilovolt protons (after Cockcroft and Walton).

set to whirling in a magnetic field between two semicircular electrodes by the successive timed application of a relatively low high-frequency voltage applied between the two electrodes. By this means they produce protons of over 2,000,000 volts energy with a high-frequency voltage of only 20 or 30 kilovolts. The curve giving the numbers of disintegrations they observed as the energy of the protons was increased is shown in Fig. 23, which also gives (as crosses) the original observations by Cockcroft and Walton.

We have very recently made observations on lithium and boron using the one-meter Van de Graaff generator and using one of the multiple-section cascade-tubes (Fig. 24) we had previously used under oil with the Tesla coil. One of the interesting observations with this equipment is that of the focussing action of such a tube, which incidentally Professor Lawrence predicted more than a year ago on the basis of his work with Sloan, but which we had not been able to test on

FIG. 23.

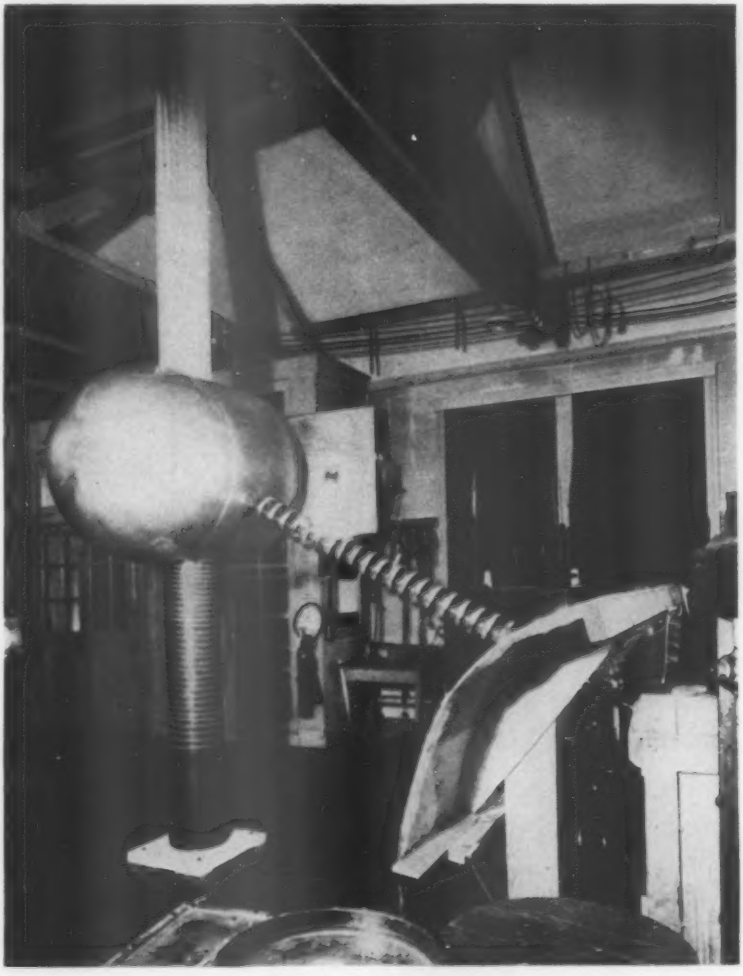


Variation in the numbers of lithium nuclei disintegrated by protons of different energies (after Henderson and Lawrence).

the fluctuating Tesla-coil voltages. Although the tube has 23 electrodes, each having a hole only 2 cm. in diameter, and is more than $1\frac{1}{2}$ meters in length, a proton-current of several tenths of a microampere from the low-voltage arc inside the high-voltage sphere is focussed 50 per cent. to 100 per cent. on the target behind the curved ground-shield where the pumps are located. Power for the hollow-anode low voltage-arc proton-source (suggested to us by Dr. E. S. Lamar) is supplied

from the silk belt which charges the sphere (200 microamperes charging current). Proton-currents exceeding 1/2 microampere give rise to too much secondary electron-emission from the poorly aligned electrodes of this tube, and a larger 6-section tube is now being installed for heavier

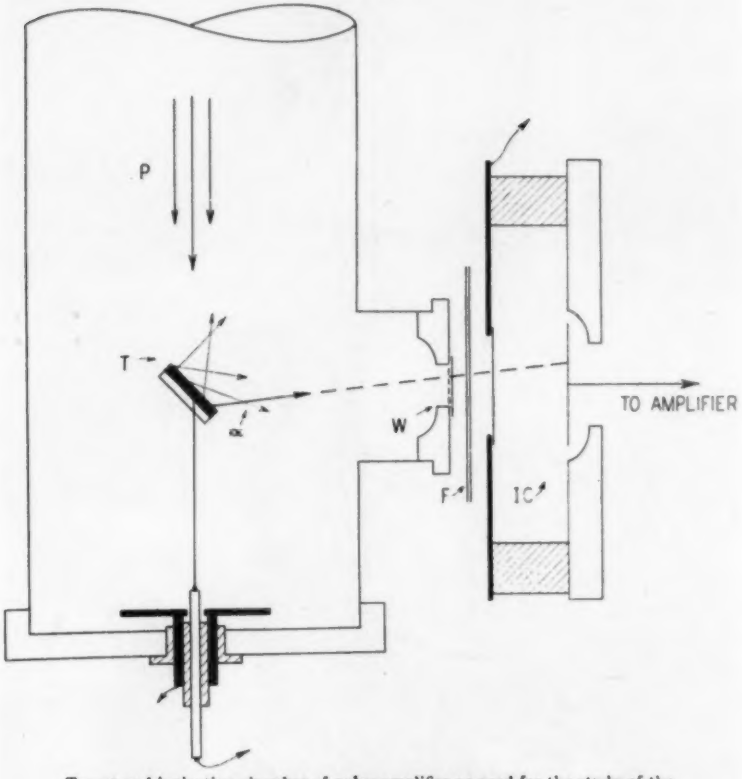
FIG. 24.



One-meter generator and cascade-tube used at the Department of Terrestrial Magnetism to study the disintegration of lithium and boron.

target-currents. This generator reaches a (positive) potential of 600 kilovolts under nearly all conditions (of weather and other factors) and has been used as high as 750 kilovolts. The voltages are measured by a generating voltmeter as used by Gunn and by Kirkpatrick (seen in the large aluminium sheet against the instrument-case on the far side of the photograph of Fig. 24) and have been checked by sparks to a two-meter sphere and roughly checked by magnetic deflection of the proton-beam.

FIG. 25.



Target and ionization-chamber of pulse-amplifier as used for the study of the disintegration of lithium and boron.

The target-arrangement is similar to that used by Cockcroft and Walton, as shown in Fig. 25. The alpha-particles produced by the disintegrating nuclei pass through a thin

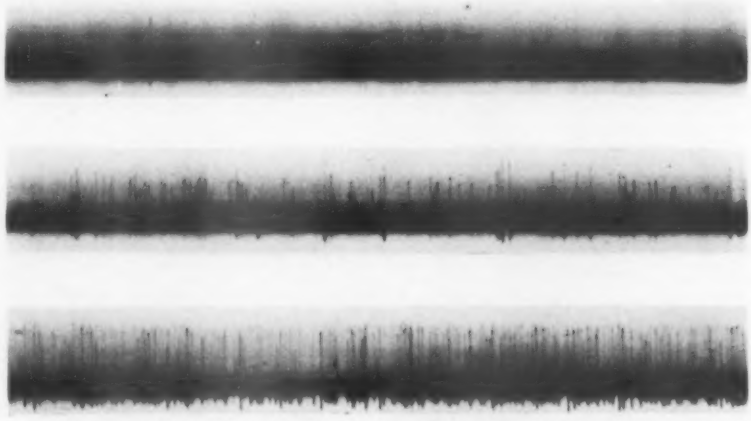
(4-mm. stopping-power) mica window, through foils which are used to measure their range, and into the ionization-chamber of the amplifier of Fig. 6, which is used for all of our observations.

FIG. 26.

Pulse-amplifier record showing disintegration alpha-particles from lithium target; length of trace shown approximately one minute.

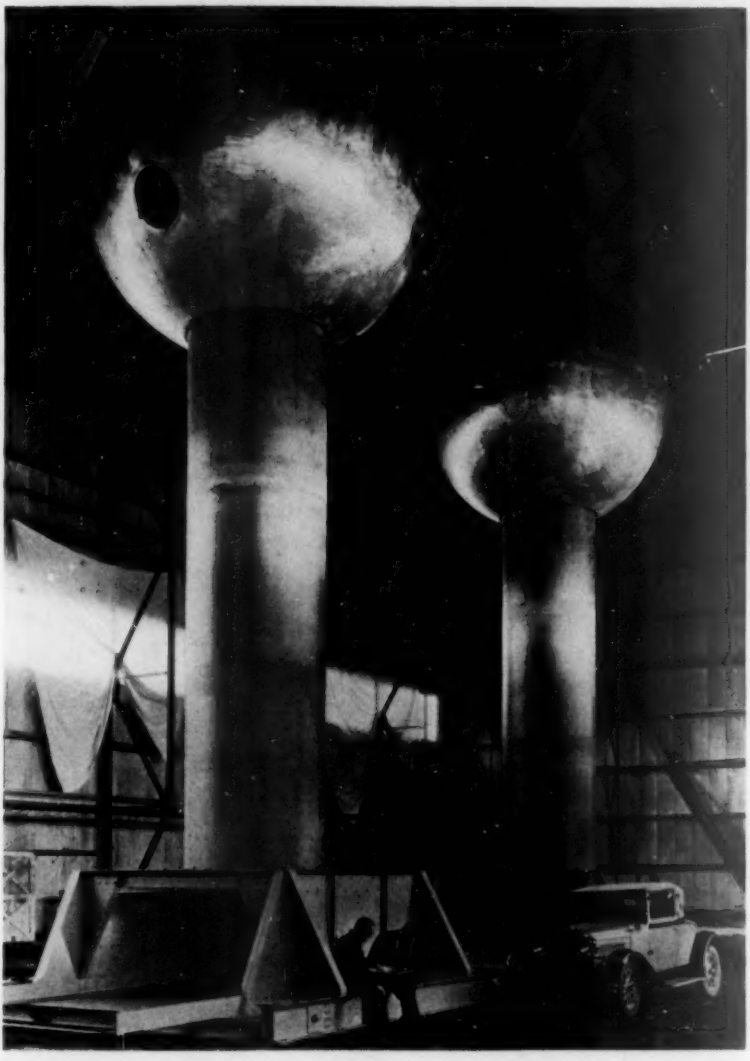
A record showing the disintegration of alpha-particles from a lithium target is shown in Fig. 26, and Fig. 27 shows several such records on boron, with different thicknesses of foils interposed before the ionization-chamber. We find that lithium gives rise to two ranges of particles, the shorter just under 2 cm.; and boron also emits two groups of alpha-particles, the shorter being somewhat under 3 cm. range. The total number of particles observed from boron is roughly 20 times the number from lithium, and, assuming uniform

FIG. 27.



Pulse-amplifier records for boron target with various foils interposed for measurement of the range of the disintegration alpha-particles; upper trace, stopping-power 31 mm.; middle trace, stopping-power 23 mm.; and lower trace, stopping-power 12 mm.

FIG. 28.



Fifteen-foot diameter generators being assembled by Dr. Van de Graaff and his colleagues at the Massachusetts Institute of Technology, Round Hill Experiment Station.

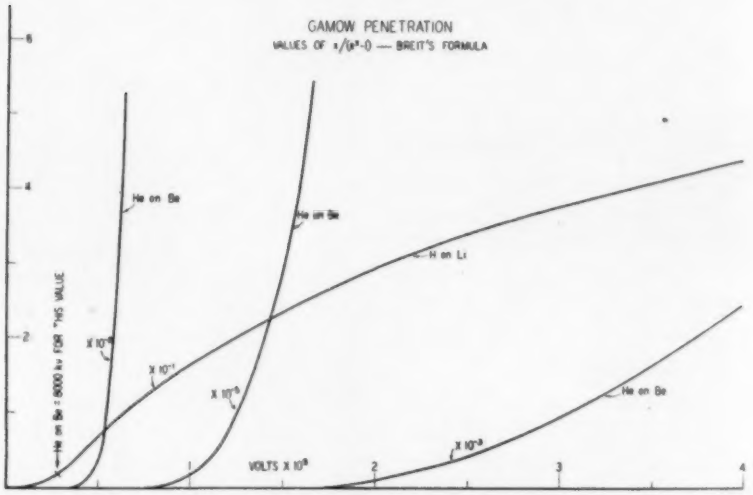
distribution of the proton-beam over the target, our data indicate that one boron nucleus disintegrates for about 4,000,000 protons, striking the target with an energy of 600 electron-kilovolts. While we were in the midst of these observations, Cockcroft and Walton published new results for boron and lithium in *Nature* which are in essential agreement with these figures.

Before leaving the discussion of the Van de Graaff generator, I take pleasure in showing a photograph (Fig. 28) which Dr. Van de Graaff just sent us of the two 15-foot generators he and his colleagues are building at the Massachusetts Institute of Technology experiment-station on Colonel Green's estate at Round Hill, Massachusetts. They estimate that a potential-difference exceeding 8,000,000 volts will be obtainable between these two spheres. To indicate the tremendous possibilities of this magnificent installation in its application to nuclear physics, I shall turn very briefly to the predictions of nuclear theory before concluding this discussion.

Although the experiments in Cambridge have cast serious doubt on the validity of the theory, I shall indicate the predictions of the only theory that as yet exists for the consideration of problems involving the penetration of atomic nuclei by particles approaching its boundaries (from the inside or from the outside)—the wave-mechanics theory mentioned earlier in the evening. Gamow gave a formula in 1928 for the probability of the penetration of a nucleus of atomic number Z by a particle of atomic number Z'. In Fig. 29 we have plotted this probability of penetration, using a modified form of Gamow's equation published by Breit in 1929, for two particular types of nuclear collision, protons on lithium ($ZZ' = 3$) and helium ions on beryllium ($ZZ' = 8$), with the energy of the bombarding particles as the abscissæ. Note that the curve for H on Li has already become very flat, the probability of penetration approaching unity, at even 1,000,000 volts. The type of curve marked "H on Li" is perfectly general for all values of Z and Z', but the exceedingly strong exponential by which the curve approaches zero at the lower voltages, and the rapidity with which the scale of voltage is shifted as the product ZZ' is increased is shown by

the curve for He on Be, which is drawn in three sections. Note that this exponential is so powerful that at 500,000 volts the probability of penetration changes by a factor of 10^{-7} in changing from $ZZ' = 3$ to $ZZ' = 8$. When it is noted that Cockcroft and Walton reported observable disintegrations for ZZ' up to 47 (Ag) and even up to 92 (U), the magnitude of the discrepancy from theoretical predictions can be faintly realized from this comparison.

FIG. 29.



Gamow curves for the probability of penetration of high-speed protons into lithium nuclei and high-speed helium ions (alpha-particles) into beryllium nuclei.

Another interesting prediction of this theory which will be exceedingly important if it is true, is the magnitude of the artificial neutron-source which may be attained by the bombardment of beryllium by singly-charged helium-ions using a high-voltage tube. From the known number of alpha-particles emitted by Chadwick's polonium-source, one can calculate directly the neutron-intensity (in terms of Chadwick's neutron-intensity) to be expected with one microampere of He^+ bombarding a beryllium target at various voltages. These figures are given in the following table:

Artificial Neutron-Source—Predicted Yields He^+ on Be.

To equal Chadwick's source requires		One microampere gives Chadwick's intensity times this factor	
265 μa	at 600 kv.	at 600 kv.	0.0038
17	800	800	0.06
.5	1200	1200	2.0
.06	1600	1600	15.1
.02	2000	2000	54.3
.0004	4000	4000	2200
.0001	5200	5200	6200
.00008	6000	6000	11800
.00003	8000	8000	34000

FIG. 30.

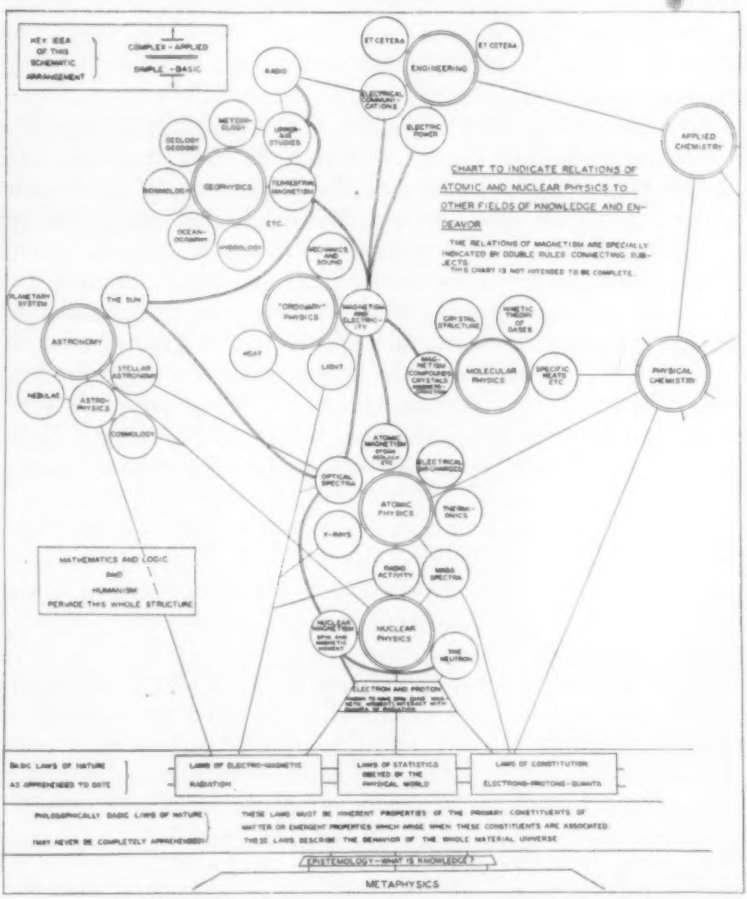


Chart indicating relations between various fields of research—necessarily and intentionally incomplete. The relations involving magnetism are indicated by double rulings.

Thus, for example, Van de Graaff's large generators bombarding a Be-target with 100 microamperes of He^+-ions at 8,000,000 volts should produce a neutron-source 3,400,000 times as powerful as the radioactive neutron-source used by Chadwick. Even our own 2-meter generator, which it is expected will operate satisfactorily at 1,500,000 volts, should provide a sufficiently strong artificial neutron-source to make possible the study of many important properties of this new structure-unit of atomic nuclei.

In closing, I shall direct your attention to the relations of this subatomic field of research to the more complex problems of more complicated fields by means of a chart (Fig. 30) which we used at the Carnegie Institution's annual exhibit of research activities December 1932. Only a few of the interrelations of the various fields are indicated, and the chart is intentionally incomplete. I should like to indicate that beyond physical chemistry, at the right of the chart, lies organic chemistry, and beyond this might be placed biology and perhaps the social sciences. Physical science is unique in that it has found a few underlying principles or laws with which all more complicated phenomena are consistent. Certainly these laws are also basic to the biological sciences, via organic chemistry, and the question arises whether there exist other laws also fundamental to the life-sciences, basic in the same sense as these fundamental laws of physics are basic. This question I take pleasure in leaving with you unanswered.

THE ANNEALING OF GLASS AS A PHYSICAL PROBLEM.

BY

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INTRODUCTION.

The variation in the properties of glass, as a result of heating or cooling, is a complex phenomenon which involves many factors. Numerous investigations during the past decade have added much to our knowledge of the nature of glass. Various properties such as viscosity, expansion coefficient, electrical conductivity, and refractive index have been studied over considerable ranges of temperature; precise measurements have been made on the anomalous changes in density and in heat absorption, which occur in a region of temperatures just below that at which the glass softens to an easily perceptible degree; the phase relations in numerous silicate systems have been investigated in great detail; and the factors that determine the formation and removal of internal stresses in glass have been measured and interrelated to an extent sufficient to put the annealing of glass on a quantitative basis.

But neither the physical nature of glass nor its chemical constitution is well understood, and there are still many unsolved problems. Numerous controversies have centered around subjects such as: (1) whether glass at low temperatures possesses the mechanical properties usually ascribed to a solid, i.e., whether it will not always deform at a finite (though possibly very small) rate when acted upon by shearing stresses; (2) whether the anomalous behavior of glass in the annealing range indicates a change of state; (3) the bearing of these anomalies on the annealing of glass; and (4) the theoretical basis for the experimentally determined relation connecting the amount of internal stress in glass and the rate at which it is released.

It is an interesting circumstance that so many lines of

inquiry should be related directly or indirectly to the annealing process. A continued accumulation of data concerning the behavior of glass in the annealing range will doubtless allow the solution of many fundamental problems regarding the glassy state. It is essential, however, that the problems be clearly defined and that any confusion between similar but unrelated phenomena be avoided. The object of this paper is to review briefly the known facts concerning the generation and removal of internal stress, to summarize the general behavior of glass in the annealing range, to present an important relation concerning the density of "strained glass," and to emphasize the necessity for distinguishing between the effects that are purely mechanical and those that are more closely related to molecular processes.

THE ANNEALING OF GLASS.

Formation of Internal Stress.—All substances when cooled from a softened to a hardened state are likely to acquire internal stresses. This behavior is more familiar in the case of glass because it is transparent and the stress can be readily detected. The words stress and strain are often used interchangeably in this connection. The usage leads to no confusion so long as the effects are elastic, since the stress (force per unit area) is nearly proportional to the strain (relative deformation), but when effects such as non-elastic deformation or viscous flow are involved, it is preferable to avoid ambiguity by using each word in its proper sense.

When a stress is applied to glass its refractive index changes, and when the stress is not purely hydrostatic the change in refractive index is different for the different directions, so that the glass becomes birefracting. The birefringence produced by stress provides a convenient means of determining the magnitudes and directions of the stresses within glass and other transparent materials, since the birefringence can be readily measured with a high precision. It has been found that for a given kind of stress, e.g., simple tension, the birefringence is proportional to the intensity of the stress. That is,

$$\Delta n = \frac{\delta}{l} = FB, \qquad (1)$$

Δn being the birefringence or difference in refractive index in the two principal directions, δ the optical path difference (usually the quantity that is directly measured), l the length of the light path through the specimen, F the stress per unit area, and B a constant called the stress-optical coefficient or the birefringence-stress ratio. For all the common glasses except those containing a very high amount of lead oxide the value of B is not far from 3×10^{-7}, if F is measured in kg./cm.^{2} That is, a tensile stress of 1 kg./cm.^{2} applied to a block of glass causes an optical path difference of about 3 mμ (millimicrons) per centimeter length.[1] The sign of the birefringence may be determined from the fact that under tension a block of ordinary glass behaves as a uniaxial optically positive crystal, i.e., γ, the greater index, is in the direction of the tensile stress.

Internal stresses are primarily dependent on the temperature gradients, past or present, within the material. They are classified as *temporary* if they are due to an existing temperature gradient, and *permanent* if due to a previous thermal condition. When a block of annealed glass at a temperature not too high is heated, it acquires temporary compressive stresses in the outer layers and tensile stresses in the interior. Conversely, if for any reason the outside of the block is cooler than the inside, and if at the same time the glass is free from stress, then removal of the temperature gradient, i.e., the equalization of the temperature, will produce compression in the outer layers and tension in the interior.

This fact has an important bearing on the formation of permanent strain in glass. Suppose that a block of glass initially at a temperature near the softening point is cooled, and in particular that its surface temperature is lowered at a uniform rate. Then, as has been shown,[2] the temperature distribution will quickly adjust itself to a parabolic curve, but in this case the establishment of the temperature gradient will not produce any temporary stress because the glass is too soft to support stress, or, what amounts to the same thing, the stress is released as fast as it is formed. Let the glass then,

[1] *Cf.* L. N. G. Filon, *Cambridge Phil. Soc. Proc.*, **12**, 313–337 (1902–1904); L. H. Adams and E. D. Williamson, *J. Wash. Acad. Sci.*, **9**, 609–623 (1919).

[2] E. D. Williamson and L. H. Adams, *Phys. Rev.*, **14**, 103 (1919).

free from stress but containing a temperature gradient, continue to cool at a uniform rate. The temperature gradient will remain (practically) constant until at some low temperature the cooling is stopped and the temperature throughout the block allowed to equalize. As stated above, the removal of the gradient will produce permanent stress, consisting of compression near the surface and tension in the middle. If the glass before it started to cool was at a temperature well below the softening-range, the formation of the temperature gradient will produce a temporary stress that will be carried down practically unchanged to room temperature. This stress being equal to the stress caused by the final removal of the temperature gradient but of opposite sign, the two sets of stresses will neutralize each other, and there will be no permanent stress. Furthermore, if the cooling had been started at an intermediate temperature (see Fig. 1) such that a part of the temporary stress was released during the early stages of cooling, the stress produced at room temperature by the removal of the gradient will predominate, and there will be permanent stress in the glass but less in amount than in the first case.

The conclusion that may be drawn from this circumstance is that the stresses in poorly annealed glass are due to the smoothing out of the temperature gradient at low temperatures, or more exactly to the part of the effect that is not neutralized by the temporary stress (of opposite sign) originally produced at the high temperature. In other words, the stress system in an unannealed glass has not arisen at high temperatures—it may actually develop at room temperature—and the stresses may be considered to be a consequence of a temperature gradient that has been "frozen in." The above statements are equivalent to the following important principle: *The permanent stress is equal and opposite in sign to the stress lost at the beginning of the cooling.* This rule has been verified for cooling glass, by direct continuous observation throughout the entire temperature range, and has formed the starting-point for a precise treatment of the annealing process.

Other explanations of the generation of internal stress in glass have been given. For example, it has been said that

when a lump of glass is cooled quickly the outside first congeals or hardens so that when the inside subsequently cools and tends to contract it is prevented from doing so by the hardened exterior, thus causing tension in the interior and (consequently) compression in the outer layers. This explanation is incomplete, and, furthermore, if a block of glass during cooling from a high temperature is observed directly it may be seen that with any reasonable rate of cooling not much stress is produced at the higher temperatures, and what little there is will be of *the opposite sign* to the final permanent strain. The formation of stress has also been ascribed, partially at least, to the anomalous volume-change (see below) known to occur at temperatures within the annealing range. While it might be expected that the large expansion-coefficient involved would have an important influence on the amount of stress produced since the stress is proportional to the expansion-coefficient, it happens that the temperature at which the anomaly is observed is too high for it to be of practical importance in this connection. Likewise, possible molecular rearrangements have not been shown to have any direct relation to the problem.

It appears that *a quantitative explanation of the formation of internal stress in a block of glass can be obtained on a purely mechanical basis*, i.e., by consideration of the relative movements, due to thermal expansion, of the various parts of the block, and that the phenomenon of internal stress has little or no bearing on the question of the physico-chemical state of glass. In this connection it is important to differentiate the three factors, birefringence, strain, and stress. As mentioned below, it is possible for glass to become birefracting (but not necessarily to acquire stress) under conditions that seem to require a consideration of the internal structure of the glass.

Release of Stress.—If stressed glass is heated to a sufficiently high temperature, the stress disappears. It has been found [3] that at any constant temperature within the usual annealing range the diminution proceeds according to the equation

$$\frac{1}{F} - \frac{1}{F_0} = ABt, \qquad (2)$$

[3] L. H. Adams and E. D. Williamson, J. FRANK. INST., **190**, 619 (1920).

in which B is the birefringence-stress ratio, A is another constant, F is the stress at any time, t, and F_0 is the initial stress. From equation (1) it follows that the relation between birefringence and time is:

$$\frac{1}{\Delta n} - \frac{1}{(\Delta n)_0} = At, \tag{3}$$

which is a relation of great practical importance because it provides an accurate representation of the data at all temperatures *at which the stress decreases at an easily measurable rate.* By differentiating equation (2) we obtain

$$-\frac{dF}{dt} = \text{constant} \times F^2. \tag{4}$$

Thus, experimentally it was found that the rate of disappearance of stress was proportional not to the stress, as had been often assumed, but to its square. The equation may be regarded as a purely empirical relation which happens to fit the data, although Preston [4] by dimensional analysis has adduced for it a theoretical foundation. This relation has evoked a considerable amount of discussion which has included adverse comment from a number of sources. At various times it has been stated: that the relation could have no physical basis [none was claimed for it by its sponsors]; that it involved special assumptions as to internal flow and the relation of strain to viscosity [no assumptions were made except that the measurements were reasonably accurate]; and that the formula was unsuitable for the representation of the data. The last objection may be answered by noting that no other relation has been discovered which would represent as well the rate at which internal stress in glass is relieved, and that the validity of the relation in question has received ample confirmation from the results of other investigators, notably the work of Hampton [5] on the annealing rate of various kinds of glass and the work of Sharp, Bailey, and Hyman [6] on the speed of disappearance of mechanically

[4] F. W. Preston, *Trans. Opt. Soc. London*, **26**, 270–273 (1925).

[5] W. M. Hampton, *Trans. Opt. Soc. London*, **26**, 14–28 (1924–1925); 27, 161–179 (1925–1926).

[6] Donald E. Sharp, James Bailey, and Irving Hyman, *J. Am. Ceram. Soc.*, **14**, 820–826 (1931).

induced stresses. It must be admitted, however, that equation (3) has been shown to be applicable only within the rather limited range of temperature and stress involved in the practical annealing of glass. At temperatures in the lower part of the annealing range very small stresses do not seem to be relieved in accordance with the equation, at least not in its original form (see below), and for extremely high stresses there are indications that the rate of release is abnormally high.

The constant A in equation (3) determines the time necessary for the annealing of glass at the given temperature. For variations in temperature over a range of at least 100° A follows the logarithmic equation [7]

$$\log A = M_1\theta - M_2, \qquad (5)$$

in which θ is the temperature and M_1 and M_2 are constants. The values of these constants are such that for most glasses A doubles for each 8° to 11° rise in temperature.

The annealing time at a given temperature depends on A and also on the initial and final stress or on initial and final birefringence. In their definition of annealing time Adams and Williamson [8] took for the final birefringence 2.5 mμ, which was one-half the allowable amount for annealed optical glass, and for the arbitrary initial birefringence 50 mμ per cm. because this was about the amount usually present in optical glass prior to the annealing process. As can be seen by a study of equation (3) the time necessary for annealing is not very much influenced by the initial stress provided the initial is several times the final stress. For example, if it takes 40 minutes to reduce the stress in a piece of glass from 50 to 2.5 units, then it would take 41 minutes if the initial stress were 100 (all other conditions being the same), and 42 minutes *if the initial stress were infinitely great* (on the assumption, of course, that the reciprocal law continued to be applicable, which, for this purpose, it would to a sufficient approximation). It would be simpler and more convenient to define the annealing time on the basis of an infinite initial

[7] L. H. Adams and E. D. Williamson, Ref. 3, p. 624. See also F. Twyman, *J. Soc. Glass Techn.*, 1, 62 (1917).

[8] Adams and Williamson, Ref. 3, p. 837.

stress and it is now proposed that this be done. The modification would not be very radical (since it involves a change of only a few per cent. in the annealing time), and it would introduce an important simplification. Whenever it became desirable to define an annealing time, t_a, at a given temperature, all that would be necessary would be to take the reciprocal of the product of A, the previously determined annealing-constant, and $(\Delta n)_a$, the prescribed final strain (in terms, for example, of birefringence). Thus,

$$t_a = \frac{1}{A(\Delta n)_a}. \qquad (6)$$

It is very important to note that an annealing time based on a definite lower limit of strain is much more generally useful than the annealing time required for the removal of a given fraction of the original strain, since the latter variety of annealing time would be nearly proportional to initial strain, while the former would be (practically) independent of it.

For each temperature (with a given kind of glass) there is a definite annealing time. Conversely the annealing temperature is determined if an annealing time has been first specified. It is important to remember that the term annealing temperature has no meaning unless the arbitrary annealing time has been chosen—which involves in turn a choice of the arbitrary lower limit of strain. Many recorded observations on the annealing of glass would have had a more permanent value if the two factors, time and "zero" strain, had been even crudely specified.

Annealing Practice.—The annealing of glass consists of two principal steps, first, the removal of the internal stress, and second, the prevention of its return upon subsequent cooling. The problem of annealing thus resolves itself into a quantitative delineation of these two factors. For the first, it is necessary to have available the data from which A, the annealing constant, can be determined at any temperature, and for the second it is necessary to formulate the relation between the permanent stress received and the conditions of cooling, by utilization of the principle stated above, viz., that the permanent stress is numerically equal to that part of the temporary stress which is lost at the beginning of

cooling. In terms of birefringence, Δn, the temporary stress in a material that is being heated or cooled at a constant rate, h, may be obtained from the equation,

$$\Delta N = 10^7 \Delta n = ch. \qquad (7)$$

Here, ΔN is the relative path difference in mμ per cm., and c is a constant for a given specimen but varies with the material and in general is proportional to the square of the size. For a slab or disk of optical crown glass or of plate glass, of thickness 2a, viewed longitudinally along the middle, $c = 13a^2$ if a is expressed in centimeters, h in deg. C per min., and ΔN in mμ per cm.;[9] for Pyrex glass c is equal to about $3a^2$ under the same conditions; and for silica glass c is equal to about $0.6a^2$.

According to the older method of annealing, the glass was heated to a temperature such that the strain disappeared almost instantly and was then cooled very slowly, but the same end may be accomplished by holding the glass at a much lower temperature until it is (practically) free from strain and then cooling at a comparatively rapid rate. It has been demonstrated mathematically and confirmed experimentally[10] that the second method is highly advantageous. Furthermore, if c is known and A has been determined at various temperatures, and if, in addition, the standard of annealing [i.e., the allowable final birefringence $(\Delta n)_s$] has been specified, it becomes possible to state in exact terms the conditions under which a prescribed degree of annealing can be accomplished in minimum time. These conditions were given by Adams and Williamson in the paper already cited,

[9] The complete definition is as follows:

$$c = 10^7 \frac{\alpha B a^2}{6\kappa(1/6R + 2/9K)},$$

in which α is the coefficient of linear expansion, B is the birefringence-stress ratio, κ is the thermal diffusivity, R is the rigidity, and K is the bulk modulus (see Ref. 3, p. 862).

The values of c as given are intended to be only approximate but are calculated from the best data available in the literature. A calculation by Dr. G. V. McCauley (personal communication to the author), utilizing some unpublished data on the physical constants of Pyrex glass, indicates that c for this material is about 25 per cent. higher than the value given above.

[10] Adams and Williamson, Ref. 3, pp. 850, 853.

and have proved to be of practical value in the annealing of glass. The principles that were outlined provide the means for taking account of variations in the kind of glass and in the size of article, and have been applied with notable success to the annealing of large telescope lenses.[11]

The modification in the definition of annealing time, noted above, allows an important simplification in the determination of the proper procedure for annealing. The revised procedure for annealing is as follows: the glass is held at a temperature θ_0, such that A has the value,

$$A_0 = \frac{1}{20c} \tag{8}$$

for a time, in minutes,

$$t_a = \frac{40c}{(\Delta n)_s} \tag{9}$$

and then cooled at a rate which initially is $(\Delta n)_s/c$ and which increases, as the temperature is lowered, according to the equation,

$$h = \frac{(\Delta n)_s}{2c}\,(1 + 2^{(\theta_0-\theta)/20}). \tag{10}$$

The cooling-rate after the temperature has dropped through successive 10° intervals is respectively 1.2, 1.5, 1.9, 2.5, 3.3, 4.5, 6.1, 8.5, and so on, times the initial rate. In actual practice little time is saved by continuing to increase the rate after it has become very high, and in any case the maximum cooling rate is limited to about $200/c$ (corresponding to a stress of about 1/4 of the breaking strength), if danger of breakage, on account of high temporary stresses, is to be avoided.

Under the conditions laid down the strain in the glass is reduced at the annealing temperature to $\frac{1}{2}(\Delta n)_s$ and a like amount is then allowed to enter during the cooling process, the final strain thus being $(\Delta n)_s$. Moreover, the annealing-time is equal to the (ideal) cooling-time,[12] and the total time

[11] See, for example, A. N. Finn, *Bur. Stds. Jour. Res.*, **3**, 325 (1929).

[12] We have, $t_a = t_c = \frac{2}{A_0(\Delta n)_s} = \frac{40}{h_0} = \frac{40c}{(\Delta n)_s}$.

(in minutes) for the complete operation is $80c/(\Delta n)_s$. Since c varies as a^2 it is evident that the time required for annealing a piece of glass increases rapidly with the size of the article; increasing the thickness of a disk by a factor of 10 would increase the annealing time by a factor of 100 (and would require a lowering of the annealing temperature by about 65°).

Circumstances may arise that make it inexpedient to carry out the annealing at exactly the optimum temperature, i.e., at the temperature for which $A = 1/20c$. In that case, the annealing temperature θ' (or the corresponding A') is selected, and a value is chosen for $(\Delta n)_a$ (that part of $(\Delta n)_s$ which it is desired to leave in the glass just before the cooling begins, the remainder, $(\Delta n)_c$, being acquired during the cooling), whereupon the glass is held at θ' for the time,

$$t_a = \frac{1}{A'(\Delta n)_a} \tag{11}$$

and then cooled at the rate,

$$h = \frac{(\Delta n)_c}{20c^2A}\,(1 + 2^{(\theta'-\theta)/20}). \tag{12}$$

In this more general [13] case the cooling time is

$$t_c = \frac{400c^2A'}{(\Delta n)_c}. \tag{13}$$

If we retain the condition that $(\Delta n)_a = (\Delta n)_c$ (but not necessarily that $t_a = t_c$) we find that a small change in θ, above or below θ_0, makes a considerable change in the total time required; a change of 10°, 20°, or 30° in either direction increases the time by the factor, 1.25, 2.1, or 4.1 respectively.

On the other hand, the most favorable value for $(\Delta n)_a$ for a given θ may be found by writing from (11) and (13) an expression for t, the sum of t_a and t_c, and setting $dt/d(\Delta n)_a$ equal to zero. In this way we find that for a predetermined temperature, the glass should be held at this temperature for a time such that $(\Delta n)_a$ will have the value,

$$(\Delta n)_a = \frac{(\Delta n)_s}{1 + 20cA}. \tag{14}$$

[13] It may be noted that application of the conditions, $A' = 1/20c = A_0$ and $(\Delta n)_a = (\Delta n)_c$ (θ' then becoming θ_0) reduces equations (11) and (12) to (9) and (10) respectively.

It may be observed that when $A = 1/20c$, as is the case at θ_0, equation (14) reduces to $(\Delta n)_a = (\Delta n)_s/2$. It is preferable to anneal at the optimum temperature, θ_0, whenever practicable, but if for any reason this is not desirable, then the annealing time at the chosen temperature should be determined by means of equations (11) and (14), and the cooling rate by equation (12). Under these conditions the total time required, if θ' is 10°, 20°, or 30° in either direction from θ_0 (the optimum temperature), will be 1.12, 1.5 or 2.5 respectively, times that required under the most favorable circumstances.

The equations just given involve the temperature interval for which the annealing constant doubles. For the sake of simplicity this interval has been taken as 10°, which is not far from the actual value for all ordinary glasses. The author is indebted to Dr. G. V. McCauley for the suggestion that these equations be made more general by letting p denote the temperature interval in which A doubles. Equations (8) and (9) respectively then take the form,

$$A_0 = \frac{1}{2pc}, \tag{8a}$$

$$t_a = \frac{4pc}{(\Delta n)_s}. \tag{9a}$$

In this more general case the cooling-rate after the temperature has dropped through successive intervals of p degrees may be readily calculated from the equation,

$$h = \frac{(\Delta n)_s}{2c}\left(1 + 2^{(\theta_0-\theta)/2p}\right). \tag{10a}$$

In practice more attention should be paid to the actual cooling-rate at various temperatures than to the time-temperature curve, but this curve may be evaluated directly from the integrated form of (10a), viz.,

$$t = \frac{4pc}{(\Delta n)_s}\left[\frac{\theta_0 - \theta}{2p} - \frac{\log\left(1 + 2^{(\theta_0-\theta)/2p}\right)}{\log 2} + 1\right]. \tag{10b}$$

Moreover equations (12), (13), and (14) take the form, respectively,

$$h = \frac{(\Delta n)_c}{2pc^2A'}(1 + 2^{(\theta'-\theta)/2p}), \tag{12a}$$

$$t_c = \frac{4p^2c^2A'}{(\Delta n)_c}, \tag{13a}$$

$$(\Delta n)_a = \frac{(\Delta n)_s}{1 + 2pcA'}. \tag{14a}$$

As an example of the application of the above principles let us consider an interesting problem, namely, the annealing procedure for a disk of Pyrex glass, 200 inches in diameter and 30 inches thick. Of the dimensions, only one, the thickness, is important in this connection. The semi-thickness, a, is 38 cm., and a^2 is 1,440. Therefore, c, which for Pyrex glass has been taken as $3a^2$, equals 4,300. If the permissible strain is to correspond to 5 mμ/cm. along the middle, then by equation (9) the annealing time is 34,400 minutes or 24 days. Hence, the disk after being cast and allowed to cool down rather rapidly to the annealing temperature is held at that temperature for 24 days, whereupon the temperature is allowed to fall, slowly at first, and then more rapidly. The cooling rate, in this critical stage of the process, by equation (10) is initially 0.03° per hour and as the temperature is lowered increases in accordance with the equation until the maximum safe cooling rate is attained. This is about $200/c$, or 8° per hour, and represents the rate at which the subsequent cooling might proceed with a moderate factor of safety, although it would in some instances be preferable to limit the maximum cooling-rate to one-third of this amount, which would give a larger factor of safety without increasing very materially the total cooling time. Since the cooling time is practically the same as the annealing time, the total time for the annealing process would be about 50 days.

If the final strain along the middle is to be not 5 but 10 mμ/cm., which has been thought by a number of investigators to be permissible for optical glass, then the total time required would be one-half as long, or 25 days. On the other hand, in actual practice it would be advisable to allow for the effect of unavoidable irregularities in the temperature control by applying a factor of safety of 2. In this case the

glass would be held at the annealing temperature for twice the theoretical time and would be cooled at one-half the theoretical rate. This would double the total time, so that the total time required for the annealing process would be 100 days for a final strain of 5 mμ/cm., and half this long for a final strain of 10 mμ/cm. The factor of safety of 2 possibly may not be necessary with carefully designed automatic electrical control.

The annealing temperature, θ_0, can not at present be estimated accurately, because there are no published quantitative data on the annealing constant A of Pyrex glass. If the values of A for this glass at various temperatures were known, the proper annealing temperature for the disk under consideration could be determined by means of equation (8). A rough estimate of this temperature can be obtained from the observations by Littleton and Roberts [14] on the time at which practically all the strain disappears at a given temperature, and turns out to be around 450°. Recent unpublished work by various investigators (personal communication from Dr. McCauley) indicates that this temperature would be more nearly 470°. Attention is directed to the fact that from a knowledge of the physical constants of a glass it is possible to calculate the annealing *time* for a piece of a given size, even though the annealing constant—which determines the annealing *temperature*—may not be known.

It is also of interest to note the best procedure for annealing this disk if it be desired to anneal it at a temperature 20° higher than θ_0, say 490°. Under these circumstances the best value of $(\Delta n)_a$ is determined by equation (14), and is found to be 1 mμ/cm. if $(\Delta n)_s$ is 5 mμ/cm. The annealing time by equation (11) is 15 days; the initial cooling rate by equation (12) is 0.01_2° per hour; and the (ideal) cooling time by equation (13) is 60 days. The total time required is 75 days, or 50 per cent. longer than the time required when, for the same $(\Delta n)_s$, the annealing is carried out at the optimum temperature.

It should be noted that taking a 25 per cent. higher value of c, as mentioned above, would increase these various time

[14] J. T. Littleton and E. H. Roberts, *Jour. Opt. Soc. Amer.*, 4, 224–229 (1929).

intervals and decrease the cooling rates in like proportion. The above annealing schedules are for illustrative purposes only and might be subject to considerable revision if more precise values of the various physical properties involved were available. It would be unprofitable to attempt to anneal a very large piece of glass without first securing better data on some of these physical properties.

In any intelligent application of the principles governing the annealing of glass, it is essential for each of the factors involved to be determined or specified in exact terms. A knowledge of the annealing constant, A, at various temperatures, of course, is necessary, and it is equally important that the required degree of annealing be stated quantitatively (which does not mean that ridiculously low or narrow limits need to be specified). The total time actually required for annealing is nearly inversely proportional to the permissible strain. It is evident, therefore, that it would be difficult to attempt to make an annealing procedure meet a specification such as "fairly well annealed" or "annealed so as to cut readily" unless the strain pertaining to these conditions had first been placed within definite limits. As an illustration of the wide range of times required for annealing it may be noted that it takes about 100 times as long to anneal a 20 mm. sheet down to 15 mμ/cm. as to anneal a 6 mm. sheet down to 150 mμ/cm. Instances in which it has been reported that the expected annealing-time did not agree with that actually required may possibly indicate that the quantity, A, is not quite constant (at a given temperature), being larger for very high stresses; but, more probably, the apparent lack of agreement is due to uncertainties in the standard of annealing.

THE VITREOUS STATE.

Anomalies in the Annealing Range.—For most purposes a glass may be regarded as merely an undercooled liquid. As the temperature is lowered the material changes gradually and continuously from a mobile to a hard, brittle state. In studies of phase equilibrium in various systems there is no need to distinguish between thin liquids and typical glasses—the essential differences in behavior are connected with viscosity, and are differences of degree rather than kind.

And yet at low temperatures the properties of a glass (except crystallinity) are, from the "common-sense" point of view, those of a nearly perfect solid, even though from the standpoint of its genesis and stability it is fundamentally a liquid. This somewhat paradoxical situation has been made more interesting by the results of numerous careful investigations, which have established the existence of certain anomalies occurring at temperatures in the annealing range and therefore near the softening range. These anomalies resemble the discontinuities associated with recognized transformation-points, but are much less noticeable (except in the case of specific heat, which, for some materials, increases by more than 50 per cent. in passing through the softening range), and are spread out over an ill-defined temperature interval.

One of the most striking effects is the heat absorption observed upon heating glass at temperatures near the upper end of the annealing range.[15] The effect is a reversible one (unless the temperature is changed too rapidly), an equal quantity of heat being evolved upon cooling, in about the same temperature interval. Furthermore, the effect is not peculiar to silicate glasses but probably is common to glasses of all kinds, organic as well as inorganic. The heat absorption may be easily measured with a thermocouple, and has formed the basis of a method proposed by Tool and Valasek [16] for estimating the "annealing temperature" of glass.

The anomalous change in volume, which occurs in this same critical range, has also been thoroughly investigated, and has been found to amount to as much as 0.02 in specific volume or in density. Like the thermal effect it is reversible if the temperature is changed slowly. But the deficiency in density found in temperatures above the critical range may be carried down to low temperatures by rapid cooling.[17] It is as if a shift in an equilibrium state took place within a rather narrow temperature interval and the equilibrium state adjusted itself so slowly that it could be readily quenched.

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[15] A. Q. Tool and C. G. Eichlin, *J. Opt. Soc. Amer.*, **4**, 340 (1920); **8**, 419 (1924); *J. Am. Ceram. Soc.*, **14**, 276 (1931); *Bur. Stds. Jour. Res.*, **6**, 523 (1931).

[16] A. Q. Tool and J. Valasek, Bur. Stds. Sci. Papers No. 358 (1920).

[17] A. Q. Tool, D. B. Lloyd, and G. E. Merritt, *J. Am. Ceram. Soc.*, **13**, 627–646 (1930).

Other properties such as specific heat, refractive index, and electrical conductivity show similar anomalies in the annealing range. On several occasions it has been suggested that the anomalous behavior of glass, especially with respect to the heat- and volume-changes, at just those temperatures for which the internal stress is relieved at an easily measurable rate had an important bearing on the annealing problem and might even be the dominant factor in determining the amount of permanent stress remaining after a given thermal treatment, but it has been demonstrated [18] that the permanent stress may be accurately calculated from (1) the temporary stress due to temperature gradients and (2) the rate of release of the stress at various temperatures, and that the irregularities in the critical range do not need to be considered in this connection.

The anomalies mentioned change rapidly in the annealing range. The temperatures (*a*) at which internal stresses decrease rapidly and the temperatures (*b*) at which properties such as density or refractive index tend rapidly toward equilibrium values are about the same, but there is no obvious causal relationship between internal stress on the one hand, and anomalous density or refractive index on the other. Certainly the mean density of a block of glass is not affected by any system of internal stresses (see below). Refractive index and density, however, are known to be closely related. It is evident, therefore, that the refractive index, as measured by light passing through the entire block, will not be directly related to internal stress, but will be practically independent of it, although in various parts of the block the local effects due to compression or tension will be superimposed on the (usually) much larger index anomaly. If the original block be broken or cut up into smaller pieces the stresses in each piece will readjust themselves (and incidentally take on a smaller average value) so that the condition of constant mean density and of practically constant mean index will still be fulfilled.

The independence of the anomalies and the internal stresses (except in so far as they change in accordance with the intrinsic mobility of units of structure, although not

[18] See, for example, p. 868 of Ref. 3.

necessarily the same unit, or at the same rate) is very important but does not seem to have been well understood. The failure to differentiate between the two sets of phenomena has been the cause of much confusion and probably accounts for the existence of a large number of mistaken notions to be found in various papers on the subject of glass. As an example of an unusually complicated variety of misapprehension the following passage from a paper by Berger [19] is quoted.

> "This variability [in various properties] is generally explained as being due to strain in the glass. According to L. H. Adams and E. D. Williamson, the way this strain arises is that the differences of length which appear during the cooling process are more or less levelled out through the flow of the glass, but reappear to the same extent at the ordinary temperature and become visible in the permanent double refraction. From the usual purely mechanical-physical point of view, therefore, viscosity, strain, and dependence of properties on the previous history seem to be closely connected.
>
> "But a whole series of observations contradicts the correctness of this explanation. According to Adams and Williamson's theory, for instance, a state of compression should prevail at the outer surface of a rapidly cooled glass, and this compression ought to increase the refraction. This was usually measured by the Pulfrich refractometer, which effectively indicates the refraction for the surface only. The result was not an *increase*, but, as already stated, an appreciable *decrease*. If, on the other hand, glass in a state of stress is pulverised, the double refraction largely disappears, but the lower value of the refraction and density remains almost unaltered. Further, A. I. Stojaroff was able to show that when the temperature is kept constant above the softening point (when, according to Adams and Williamson, no strain should arise) the refraction distinctly changes, moving in opposite directions, according as a value of higher or lower refraction is taken as starting point."

[19] E. Berger, *J. Soc. Glass Techn.*, **14**, 280 (1930).

Although the fallacies in this statement may be self-evident it seems desirable to make the following comments: (1) The variability may have been explained as being due to strain, but Adams and Williamson did not so explain it. (2) The "purely mechanical-physical point of view" requires no relationship between the strain and the dependence of various properties on thermal history. (3) The conclusion by Adams and Williamson that a definitely predictable compression exists in the outer layers of a block of glass cooled in a given way (this compression then causing an increase in the refractive index) is not contradicted by the well-known fact that the surface as well as the interior of quickly cooled glass may be abnormally low in index, since two separate but superimposed effects are involved. (4) Similarly, the statement that at temperatures above the softening point, a change of the refraction toward its equilibrium value may be observed is irrelevant for reasons already given.

The true nature of the anomalies of glass in the critical range is not yet well understood, although much attention has been given to the subject. It has been suggested that, since the effects under consideration resemble to some extent the effects associated with transformation points, the critical range may indicate a transition from the ordinary liquid state to an entirely different state,[20] which is designated as the vitreous or the glassy state. This condition has been considered to be sufficiently different from any of the other recognized states to justify calling it a fourth state of matter.

The explanations that have been offered for the supposed transition are as ingenious as they are numerous. A favorite type of theory presupposes a sudden change in dissociation or in association or in polymerization or in state of aggregation. A transformation from strained to unstrained molecules has also been suggested. Lebedeff [21] considered the anomalous behavior of silicate glasses, which often occurs in the region between 500° and 600°, to be connected with the $\alpha - \beta$ inversion in minute quartz crystallites remaining in the glass, and concluded that the function of annealing is not so much

[20] See, for example, Parks and Huffman, *Science*, **64**, 363 (1926); Berger, *Z. techn. Phys.*, 1931, 344–363.

[21] A. A. Lebedeff, *Trans. Opt. Inst. Petrograd*, **2**, No. 10 (1921).

the removal of stresses as the attainment of complete polymorphic transformation. Another picture of the constitution of glass has been presented by Filon and Harris,[22] who observed that when glass under external load was cooled even very slowly from a high temperature the glass was birefracting. They quite correctly concluded that under certain conditions glass may show birefringence although free from stress, and then reasoned that the material could not be homogeneous but must consist of at least two phases. According to this view birefringence may arise from "cryptostresses" due to the mechanical interaction of an elastic and a viscous phase.

There does not seem to have been as yet any entirely complete and convincing explanation of the peculiarities of matter in the vitreous state. We may have something approaching the character of a change of state, although of a very mild variety and unlike any recognized true transition, and we may have molecular rearrangements that allow glass to take on a birefracting unstressed condition; but not much more can be said, and probably not much progress can be made, until it becomes possible to determine the atomic and molecular configuration in glasses as has already been done with crystalline solids.

Effect of Internal Stress on Density.—It has been believed by many investigators that the variations in density and other properties of glass caused by heat treatment were directly connected with the magnitude of the internal stresses and that the disappearance of the anomalies was coincident with the relaxation of the internal stresses during annealing. But various circumstances, such as the fact that cutting up a block of glass having abnormally low index into smaller pieces leaves the index and density practically unchanged while materially reducing the internal stress, cast doubt on the above supposition. Moreover, as stated by Tool and Hill [23] in 1925, "Much of the change both in index and density occurs, however, when there can be no doubt regarding the non-existence of any appreciable mechanical strains . . . either before, during, or after the heat treatment producing

[22] L. N. G. Filon and F. C. Harris, *Proc. Roy. Soc.*, **103**, 561–571 (1923).

[23] A. Q. Tool and E. E. Hill, *J. Soc. Glass Techn.*, **9**, 195 (1925).

it." It is of interest to investigate this question more thoroughly, and to determine exactly the effect of a system of internal forces on the density or on the total volume of a piece of glass.

Let us take first a special case, namely, that of a sphere of radius a, which has been strained by cooling it at a constant rate, h, through the annealing range. In this case the radial stress F_r at any distance r from the center is given by the equation,[24]

$$F_r = C(a^2 - r^2) \tag{15}$$

and the tangential stress F_t by the equation,

$$F_t = C(a^2 - 2r^2), \tag{16}$$

in which C is a factor depending on h and also on the expansion-coefficient, the thermal diffusivity, and also on the elastic constants of the material. The total volume-change, ΔV, due to stress, may be calculated from P, the hydrostatic pressure, at any point by the relation,

$$\Delta V = \frac{4\pi}{K}\int_0^a Pr^2 dr, \tag{17}$$

in which K is the bulk modulus. The hydrostatic component is equal to one-third the sum of the principal stresses, and therefore

$$P = \frac{F_r + 2F_t}{3} = \frac{C}{3}(3a^2 - 5r^2). \tag{18}$$

Substituting in equation (17) and integrating, we have

$$\Delta V = \frac{4\pi C}{3K}\int_0^a (3a^2r^2 - 5r^2)dr = 0. \tag{19}$$

That is, in this special case, the volume-change is zero.

Of greater value is a consideration of the general case, for any system of forces in a body of any shape. In this instance we use the principle of static equilibrium, viz., that the algebraic sum of all the tractions normal to any plane is zero. That is,

$$\int X dy dz = 0, \qquad \int Y dx dz = 0, \qquad \int Z dx dy = 0, \tag{20}$$

[24] Ref. 3, p. 862.

X, Y, and Z being the tractions at any point parallel respectively to the directions x, y, and z.

For the total volume change we have

$$\Delta V = \int \frac{X + Y + Z}{3K} dxdydz. \qquad (21)$$

Expanding and substituting the equalities of (20), we find

$$\Delta V = 0. \qquad (22)$$

That is, in the most general case any set of internal stresses, of any magnitude whatever, produces no change in the total volume or in the average density. In unannealed glass the stresses near the center are usually predominantly tensile and therefore near the center the density may be less than the average; moreover, near the surface compressive stresses predominate, and the density may be greater than the average. But the deficiency in density in the interior bears just the right relation to the excess of density in the outer portions so that the mean density of the whole piece is exactly the same as if the glass were free from stresses. That is to say, although in a specimen of unannealed glass there are stresses that may be very high, and although such glass usually has an abnormally low density, the stresses in themselves have nothing to do with the deficiency in density.

Viscosity and Rigidity.—Many of the questions that have arisen concerning matter in the glassy state would become much less difficult if the connection between viscosity and rigidity were clearly understood. Both factors involve shearing stresses (that is, stresses tending to move adjacent planes relative to each other and in a direction parallel to themselves) and shearing strains or shears, but one is an elastic and the other a non-elastic effect. Rigidity, R, is defined as the ratio of F_s, the shearing stress per unit area, to the elastic and reversible deformation. That is,

$$R = \frac{F_s}{dv/dx}, \qquad (23a)$$

in which x denotes the distance along one axis of reference and v the corresponding displacement in the y-direction, the

stresses being in planes parallel to the z-direction. The shear, dv/dx, may be expressed in other terms; it is equal to $\Delta\vartheta$, the change in angle between adjacent sides of a square that has been distorted into a rhombus, and is also equal to $2\Delta l/l$, that is, twice the relative change in length of either diagonal of the original square. Viscosity, η, is defined in terms of permanent deformation or flow, as follows:

$$\eta = \frac{F_s}{d\dot{v}/dx}. \tag{23b}$$

Here $\dot{v}$ is the time-rate of change of the displacement v, that is, the velocity of a plane at the distance x from the reference plane.

There is no sharp dividing line between elastic and viscous materials. Some of the most perfectly elastic solids may be made to flow if the stress is sufficiently high, and moderately mobile substances like pitch exhibit an obvious rigidity, which may be measured by twisting or bending a rod of the material and determining how much it springs back. Elastic bodies are not elastic because of a high rigidity; they are called elastic because, the viscosity being very great, their elasticity [25] is easy to observe. On the other hand, fluid bodies are so classified because they have a low viscosity but not necessarily a vanishing rigidity. The elastic deformation decays at a rate nearly proportional to the mobility, so that with ordinary fluids the observation and measurement of the rigidity is difficult, but it is not inconceivable that thin liquids and even gases have a measurable rigidity, although special methods would be required in order to detect it. The measurement of the rigidity of glass in the softening range would be of great interest. It is very desirable to know something of the relation between viscosity and rigidity in the temperature range in which both can be readily measured, and especially the relative rates at which they change as the temperature is raised.

There has been much uncertainty as to the way in which the element of time enters into the phenomena under con-

[25] We use the word elasticity here to mean resistance to change of shape not of volume.

sideration. The principal effect of the duration of the application of the stress is in connection with the accuracy of the measurements. If the time is too short, the viscosity can not be measured accurately and may appear to be infinite; if the time is too long, the determination of the rigidity may be difficult on account of a masking of the elastic effects by the permanent deformation. With periodic stresses associated with vibratory motion, the period of the vibration will depend on the elasticity, and the extent to which they are damped out will depend on the viscosity.

A complication is introduced if the material is plastic [26] (i.e., behaves as a body of infinite viscosity for stresses below a certain limit but yields steadily under stresses above this limit) or if hysteresis or elastic after-effects come into play. Furthermore, for highly viscous materials the viscosity is probably not always independent of stress.

One of the simplest ways to measure either viscosity or rigidity is by twisting a cylindrical rod. The elastic deformation, or in the case of mobile materials the elastic part of the deformation, may be used to determine the rigidity by means of the well-known relation,

$$R = \frac{2G}{\pi \varphi a^4}, \tag{24a}$$

in which a is the radius of the cylinder, φ is the angle of twist (in radians) per unit length, and G is the amount of the twisting couple.[27] By an analogous relation the viscosity, η, may be determined from the viscous yielding. From elementary principles it may be shown that

$$\eta = \frac{2G}{\pi \dot{\varphi} a^4}. \tag{24b}$$

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[26] See George F. Becker, "Finite Homogeneous Strain, Flow and Rupture of Rocks," *Bull. Geol. Soc. Amer.*, 4, 13–90 (1893).

[27] A couple consists of two equal co-planar forces in opposite directions. Its numerical measure (the moment of the couple or the torque) is defined as the product of either force and the distance between the lines along which they act. It may be noted that in a cylindrical rod under torque the shearing stress at any distance r from the axis is equal to $Rr\varphi$. Hence, by (24a), we have for the maximum shearing stress, which is at the surface, the well-known formula $F_s = 2G/\pi a^3$.

In this equation $\dot{\varphi}$ is the rate of change of φ with the time t, and the other symbols have the meaning already explained.

Littleton and Roberts [28] used the twisting of glass rods as an indirect method for estimating the annealing temperature of the glass on the assumption that the annealing rate is proportional to the viscosity, but they did not determine the viscosity in absolute units. The rate of rotation under a given torque was measured in arbitrary units and compared with the rate for a standard glass the annealing temperature of which was already known.

The similarity in the measurement of rigidity and of viscosity, which is apparent from the above equations is shown by the relations pertaining to the elongation of a rod under tension. For the elastic stretching we have the familiar equation,

$$\frac{\Delta l}{l} = F_t\left(\frac{1}{3R} + \frac{1}{9K}\right), \tag{25}$$

in which F_t is the tensile stress per unit area, K is the bulk modulus, and $\Delta l/l$ is the relative change in length. If K is very large in comparison with R (i.e., the elastic deformation is almost entirely one of shape rather than volume), equation (25) reduces to

$$R = \frac{F_t}{3\Delta l/l}. \tag{26a}$$

The analogous relation for viscous yielding may be easily derived from elementary considerations. As is well known, any tensile stress, F_t, may be resolved into three components, each of magnitude $F_t/3$, one being a hydrostatic pressure and the other being two separate shearing stresses acting along planes at 45° to the direction of the tension. Each shearing stress tends to lengthen one diagonal and shorten the other diagonal of squares whose diagonals are parallel and perpendicular to the axis of the bar. The rate of lengthening caused by each shearing stress is one-half $\Delta\dot{\vartheta}$, or one-half $\mathrm{d}\dot{v}/\mathrm{d}x$. Hence by equation (23b) this rate of lengthening is $F_s/2\eta$, and, since $F_s = F_t/3$, is also $F_t/6\eta$. The rate of lengthening due to both shearing stresses is twice this or

[28] J. T. Littleton and E. H. Roberts, *J. Opt. Soc. Amer.*, **4**, 224–229 (1920).

$F_t/3\eta$. Finally, therefore, we have

$$\eta = \frac{F_t}{3\Delta l/l}, \tag{26b}$$

in which $\Delta l/l$ is the time rate of change in length divided by the length. Comparison of this equation with (26a) again illustrates the parallelism of viscosity and rigidity. Both equations pertain to situations in which the change in volume is negligible compared to the change in shape. Many relations involving rigidity have an exact analogue involving viscosity, the principal difference being the element of time which enters into one but not the other. It is as if the mobility $(1/\eta)$ were equal to the rate at which the elastic deformability $(1/R)$ changes with time. This may have no physical meaning, but as a mathematical transformation it permits the easy conversion of equations containing η to those containing R, and vice versa.

An equation identical with (26b) was used by Trouton [29] in his investigation of the viscosity of pitch and other substances, and it formed the basis of the method by which Lillie [30] measured the viscosity of three soda-lime glasses at temperatures in the annealing range. These results Lillie combined with previous measurements at higher temperatures by the usual rotating cylinder method, and obtained a viscosity-temperature curve extending over a range of about 900°, in which range the viscosity increased by the factor 10^{12}. The line obtained by plotting log η against temperature is in general strongly curved, and somewhat less curved if log η is plotted against the reciprocal of the absolute temperature. On either plot the curvature is comparatively slight at the low temperatures, but is somewhat more noticeable in the range just above the annealing temperature. It has been held that this circumstance constitutes additional evidence bearing on the supposed transition point in glass. A careful

[29] F. T. Trouton, *Proc. Roy. Soc. London*, **77**, 426–440 (1906). The equation shows that the rate of elongation is equal to the traction or tensile stress divided by the factor 3η, which Trouton called the coefficient of viscous traction.

[30] H. R. Lillie, *J. Am. Ceram. Soc.*, **14**, 502–511 (1931). At the "annealing point," i.e., the temperature at which nearly all the strain in the glass disappears in 15 minutes, the viscosity was found to be 2.5×10^{13} poises.

examination of such curves, however, makes it seem improbable that they can supply any definite indication for or against a discontinuity or change of state.

Rate of Release of Strain.—As mentioned above, it has been found experimentally that in the annealing of glass the internal stress is relieved in accordance with the equation

$$-\frac{dF}{dt} = \text{constant} \times F^2. \tag{4}$$

That is, the stress disappears at a rate proportional to the square of the stress. Although this is to be regarded primarily as an empirical relation, Preston [31] by the application of dimensional analysis and the assumption that for a given material at a specified temperature dF/dt depends only on the stress, F, and the viscosity, η, has shown that the relation between the quantities must be

$$-\frac{dF}{dt} = k\frac{F^2}{\eta}, \tag{27}$$

k being a dimensionless constant. The empirical relation seems thus to have been given a theoretical foundation, but it may be doubted whether the problem of the release of stress has yet been solved. Although an examination of the dimensions of the various terms shows that equation (27) is dimensionally homogeneous while the equation, $-dF/dt = kF/\eta$, is not (if k is to be a dimensionless constant), and although equation (27) agrees with the experimental data, provided that η is constant (i.e., independent of F), nevertheless, it is conceivable that the use of other assumptions as to the factors on which dF/dt depends, or as to the variability of η would lead to equation (27), or to another equation of equal merit. For example, if $-dF/dt$ were equal to a constant times F/η and if η were inversely proportional to F (a not unthinkable assumption for glass of very high viscosity), then we should have a relation similar to equation (27) except that η would be replaced by η_1, the viscosity at unit stress.

[31] See Ref. 4. For the principles of dimensional analysis see also E. Buckingham, *Phil. Mag.*, **42**, 696 (1921) and P. W. Bridgman, "Dimensional Analysis," New Haven, 1922.

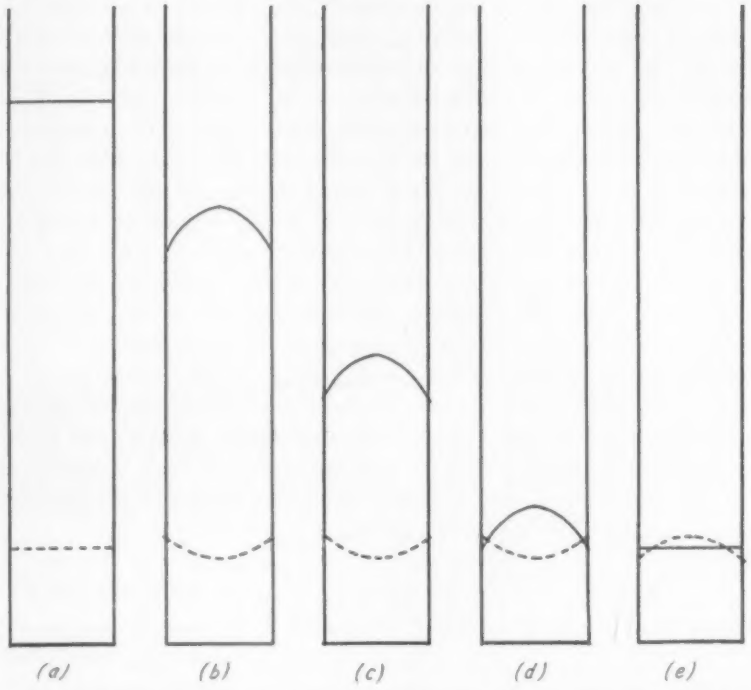
The situation is further complicated by our uncertainty as to whether viscosity really has any connection with the release of stress. Viscosity, of course, always comes into play when we are dealing with viscous flow, but it is not at all certain that release of strain is accompanied by flow in the usual sense of the word. The permanent deformation of glass, as for example by twisting or bending, involves a readily visible flow, that is, a definite and easily perceptible movement of certain planes with reference to adjacent ones (i.e., shearing motion). On the other hand, during the release of stress there may be no perceptible differential movement. For example, if stress be applied to a block of glass by clamping it between the jaws of a vise and if the temperature is such that the stress is gradually released, then probably neither the size nor the shape of the block would change as the stress disappeared. Any shearing motion would probably be of the order of magnitude of atomic dimensions.[52] In this sense, of course, the release of stress may be said to involve flow, but a distinction should be drawn between movements of directly measurable magnitude and slight movements, or readjustments, in the mean position of atoms and molecules.

If annealing does not involve flow, then there may be no simple relation between the annealing constant A and the mobility, $1/\eta$, that is, there may be no simple proportionality, although of course a functional relationship may exist. It is very suggestive, however, that both A and η vary logarithmically with temperature, and give curves with about the same slope, but we need to have more extensive data before we can determine whether the correspondence is approximate or exact.

The mechanism by which stress in glass disappears has an important bearing on the nature of the vitreous state. It is very desirable to be able to decide between the two possibilities: (1) that the effect is a *megascopic* one involving movement on a scale that is large in comparison with molecular dimensions, and (2) that the effect is a *microscopic* one, the movement being confined to slight rearrangements in the relative positions of atoms or molecules. Figure 2 is intended to illustrate, perhaps somewhat crudely, the two ways in

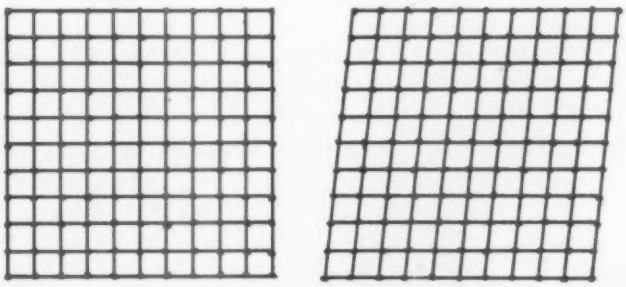
[52] See J. T. Littleton, *J. Soc. Glass Techn.* (Trans.), **15**, 288 (1931).

FIG. 1.



(After Adams and Williamson.) The ordinates represent the temperatures (solid lines) and stresses (dotted lines) in a slab of glass at several stages during cooling from an intermediate temperature, the rate of cooling being constant. The diagram illustrates the important principle that the internal stress in unannealed glass is introduced at low temperatures by the smoothing out of the temperature gradient; any stress introduced at high temperatures is of *opposite sign* to the final permanent stress.

FIG. 2.



In this two-dimensional example of a shearing strain the framework on the left is distorted into the shape shown on the right by means of a shearing stress. As explained in the text this stress may be released in two entirely different ways, only one of which involves flow in the usual sense.

which internal stress may be dissipated. The framework shown on the left consists of two sets of mutually perpendicular bars or wires soldered together at the joints. Let the square be distorted by shearing forces so that it takes the shape of a rhombus as shown on the right. In this two-dimensional case we have an example of a body under shearing stress. The stress may be relieved by allowing the framework to spring back to its original shape. This action will be accompanied by a sliding motion of the bars with reference to adjacent bars—that is, flow in the usual sense. But the state of stress may be removed by an entirely different process, namely, by allowing the solder at the joints to soften. This will bring about a stress-free condition, but without any visible motion of the parts of the framework. What movement there is will be very small in amount and confined to the interior of the joints. In the first case we have an illustration of megascopic motion and in the second an approximation to microscopic motion. The former is comparable with flow while the latter is not. At present it seems impossible to say which case corresponds to the release of stress in glass. It is interesting to note that Hampton [33] was able to determine the value of k in equation (27) by measuring A and η at the same temperature. He found that k was not equal to 1, but had a value in excess of 1,000. The significance of this is not clear.

Has Glass a Finite Strength at Any Temperature?—With regard to this problem there have been two schools of thought. According to one the mobility of a glass varies continuously with temperature. The logarithm of either the mobility or its reciprocal, the viscosity, bears an approximately linear relation to the temperature, so that the viscosity doubles for each 10° drop in temperature. Extrapolation downwards leads to the conclusion that at room temperature the viscosity of ordinary glass is at least 10^{28}, which is so great that it would be impossible to detect experimentally any flow in glass at ordinary temperatures. If the glass were stressed practically to the breaking point 10,000,000 years or more would elapse before the viscous yielding would become perceptible. Consequently the experiments that have been

[33] W. M. Hampton, *Trans. Opt. Soc. London*, **27**, 173 (1925–1926).

conducted over a period of a few days or weeks and have failed to show a permanent deformation do not supply any evidence against the supposition that at all temperatures glass has a definite, though possibly very small, mobility.

According to the other school of thought it is assumed that glass at low temperatures has a finite strength, that is, can support stresses below a given limit without any flow whatever, and therefore has the characteristic property of a solid rather than a liquid. Jeffreys [34] gives the name "durovitreous" to this state of glass. When the temperature is raised above a certain point or range the glass is supposed to pass into the "liquevitreous" state, in which state the glass is a true liquid and will flow indefinitely under any shearing stress however small, provided it is applied for a sufficient time.

We have no data which bear very directly on the question whether glass at low temperatures is an undercooled liquid or an amorphous solid. For the present the choice between the two points of view must remain a matter of opinion unhampered by experimental results, although the line of attack followed by Hampton [35] is suggestive. As mentioned in an earlier section of this paper, the "square law" for the release of stress in glass does not hold within the experimental error if the temperature is too low. The relation may be written [see equations (2) and (27)] as follows,

$$\frac{1}{F} - \frac{1}{F_0} = \frac{kt}{\eta}. \tag{28}$$

Hampton found that the results obtained by Adams and Williamson for a light flint glass were well represented at all temperatures by the expression,

$$\frac{1}{F - F'} - \frac{1}{F_0 - F'} = \frac{kt}{\eta}. \tag{29}$$

In this equation, which is a modified form of (28), F' is a constant at any given temperature and may be interpreted as a lower limit of F below which the stress will not fall even in

[34] H. Jeffreys, "The Earth," 2d ed., Cambridge, 1929, p. 183.
[35] W. M. Hampton, Ref. 33, p. 175.

infinite time. According to this equation it is the excess of F, over and above the fixed value F', that bears the reciprocal relation to the time, t. Hence the quantity F' may be considered to be the stress that the glass will support indefinitely. In other words, the glass has the finite strength, F'. The value found for F' at 300° was 6.5 kg./cm.^{2}, and at 385° was 0.8 kg./cm.^{2}, while at 400° and higher it was zero. It should be noted that the conclusions are based on the "square law," and that the fundamental applicability of this relation has not yet been established. If at the low temperatures the rate of release of stress were proportional, for example, to the fourth power of the stress the rate at low stresses would be very small and it would be difficult to determine experimentally whether the stress were tending asymptotically toward zero or toward some finite value. Additional measurements, preferably with an accuracy 10 to 50 times that attained hitherto, would throw more light on this question.

CONCLUDING REMARKS.

Although a number of practical problems relating to glass have been solved in recent years, the fundamental problems concerning the vitreous state still await solution. Progress has been retarded by the frequent confusion of similar but unrelated effects. Further progress will probably come first from the experimental side by a more thorough study of the behavior of glass in the annealing range. At present we have some scattered and incomplete data and much speculation. In the investigation of subjects as intricate as the fundamental nature of glass it is important, whenever possible, to distinguish between effects that involve molecular rearrangement and effects that are primarily mechanical, and to describe phenomena and properties in terms of things that can be measured.

SUMMARY.

The fundamental principles underlying the annealing of glass and the present state of knowledge concerning changes in the nature of glass during heating and cooling are briefly reviewed. Emphasis is placed on the fact that a quantitative explanation of the formation and removal of strain in glass, and a precise determination of the requisite conditions for

any desired degree of annealing, may be obtained on a purely mechanical basis, without consideration of the internal constitution of materials in the vitreous state.

Annealing Practice.—An improvement in the definition of annealing time (made feasible by the relatively great speed with which large strains are released) allows a considerable simplification in the determination of the proper procedure for annealing. As an illustration, the procedure for annealing a disk of Pyrex glass, 200 inches in diameter, is given. The best conditions for annealing, when for any reason the temperature must be above or below the most favorable temperature, are also discussed.

Effect of Internal Stresses on Density.—It is demonstrated that internal stresses can have no effect on the total volume or on the average density of a block of glass. The stresses may cause a deficiency in density of the interior portion and an excess near the outside, but the mean density of any large or small piece is exactly the same as if the glass were free from stress. Although unannealed glass may have an abnormally low density, the stresses themselves have nothing to do with this effect.

The Vitreous State.—The anomalies of glass in the annealing range, the relation between viscosity and rigidity, the physical basis of the rate of release of strain, and the possibility that glass at low temperatures may have a finite strength, are discussed. Although a lack of data prevents the drawing of any positive conclusions, nevertheless the state of aggregation of glass is a problem of very great interest. It appears that more attention should be given to the physicochemical side of the problem; but it is essential not to confuse phenomena that involve the internal constitution of glass with those that do not.

December, 1932.

New Method for the Purification of Enzymes.—J. STANLEY KIRK (*Jour. of Biol. Chem.*, 1933, C, 667–670) has devised a new procedure for the purification of enzymes, the use of specific anti-enzymes as precipitants. Thus the urease of the soy bean was precipitated from aqueous extracts of that bean by the addition of highly purified antiurease. Washing the precipitate with 0.4 percent. sodium chloride solution removes the antiurease. The number of urease units per gram of ash-free solids is increased 850 times by this procedure.

J. S. H.

Relationship of Fluorides in the Water Supply to Mottled Enamel.—FREDERICK S. MCKAY (*Jour. of Dental Res.*, 1933, 13, 133–134) describes conditions in Oakley, Idaho. Formerly the water supply came from a warm spring and contained 6 parts of fluoride anion per million. Persons who used this water supply during the years of enamel development uniformly developed the condition of the teeth known as mottled enamel. Seven and a half years ago, the water supply was changed; the new supply contains less than 0.5 part fluoride anion per million. New cases of mottled enamel no longer occur among the children who have used the new water supply during the period of enamel development. These findings confirm the relationship between the occurrence of this enamel defect and a high fluoride content of the drinking water.

J. S. H.

Apothecaries' Shelfware.—CHARLES H. LA WALL AND MILLICENT R. LA WALL (*Jour. Am. Pharmaceutical Asso.*, 1933, XXII, 334–345) describe a collection of 25 pharmacy jars, now the property of the Philadelphia College of Pharmacy and Science. The earliest items in the collection are of Italian origin and date to the 15th century. The entire collection is of deep interest to the student of ceramics as well as to the student of the history of pharmacy. Of the drugs and preparations mentioned on the labels, a bare half dozen are still used today.

ON THE APPLICATION OF INTERFERENCE FRINGES TO STRESS ANALYSIS.

BY

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The problem of stress analysis and its relation to the failure of materials is one of the most interesting and difficult problems of applied science to-day. It enlists the interest and labors of the engineer, physicist and mathematician. Engineers usually base their designs of structures, or machines, on *average* stresses or approximations of stresses, which are often at considerable variance with actual conditions, and compensate for it by introducing factors of safety into the working stresses based upon the accumulated experience of the profession as a whole. The development of the theory of elasticity has centered attention on the *exact* stress distribution in contrast to the average stress distribution, and has yielded valuable results. The mathematical theory of elasticity has its limitations, however, necessitating in most cases prolonged and tedious computations even for approximate results. There has, therefore, been a steady interest in, and search for an experimental method for the study of stress distributions. The most effective of the present experimental methods in two-dimensional systems at least is undoubtedly the photo-elastic method. This method is based upon the temporary double-refraction induced in a beam of polarized light passing through a stressed isotropic transparent body such as glass.

The foundation for this method was laid by David Brewster in 1816 [2] when he discovered that glass under stress exhibits bi-refringent effects. Numerous workers, notably

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[2] *Phil. Trans.* (1816), 156–178.

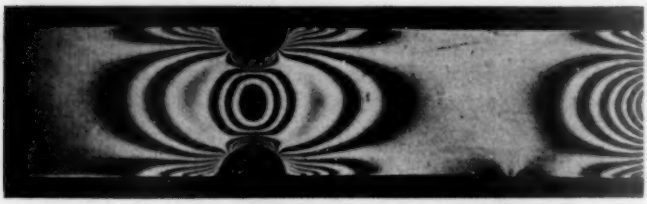
Mesnager in France,[3] Coker and Filon in England, and others [4] have perfected the mechanical and optical equipment and solved a large number of problems of scientific and practical interest. The fundamental law upon which this method is based is expressed by the equation

$$R = Ct(P - Q), \tag{1}$$

where R is the phase difference in wave-lengths between the ordinary and extra-ordinary rays, C a constant of proportionality, t the thickness of the model and P and Q the principal stresses at the point considered.

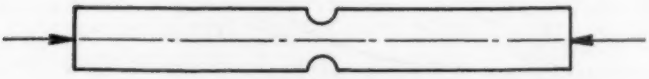
With a monochromatic source of light a stressed model produces a stress pattern which on the photographic plate consists of black fringes separated by white bands, whose shape and number is uniquely determined by the shape and dimensions of the model and the system of loading. Such a stress-pattern is shown in Fig. 1.

FIG. 1.



Stress-pattern showing $(P - Q)$ curves in bar with semicircular grooves in compression. Mode of annealed bakelite.

FIG. 2.



Sketch showing loads for Fig. 1.

When the model is free from stress the corresponding stress pattern is uniformly dark. As the loads are gradually

[3] International Association for Testing Materials, New York, 1912. (II) XXVIII. Annales des Ponts et Chaussees, 16 (1913), 133–186.

[4] For a bibliography on the subject see "A Treatise on Photo-Elasticity," by E. G. Coker and L. N. G. Filon, Cambridge University Press, 1931, pp. 695–711.

increased the field becomes illuminated except for the points at which there are no stresses, or at which the principal stresses are equal, that is at singular and isotropic points. Upon further increases in the loads the points of highest shear stress are the first to darken, and, upon additional loading, to brighten up again. Each element of the model thus alternates between complete blackness and brightness. Corresponding to a given system of loads, each point goes through a definite number of cycles of black and white. This number is of fundamental importance and is known as the *fringe order at a point.*

It follows from the stress-optic law that the value of $P - Q$ is constant along any fringe and that this value is directly proportional to the fringe order. The value of $P - Q$ corresponding to fringe of order one, or order 'n' is determined experimentally either by a pure bending, pure compression or pure tension test. Since the maximum shear equals $(P - Q)/2$ the stress pattern really gives a graphical picture of the distribution and intensities of the maximum shears in the model.

As far as the principal stresses are concerned, however, these stresses cannot be determined from the information derived from the polariscope alone. Two methods are in use to-day for the evaluation of the principal stresses: the method of graphical integration and the method of measuring deformations in a direction at right angles to the plane of the loads. The equations for the graphical integration method are due to Filon and are based upon Lame's equations of equilibrium along an isostatic curve.[5]

The suggestion to measure the lateral deformation is due to A. Mesnager,[6] who in 1913 determined from a glass model the stress distribution in a reinforced concrete bridge over the Rhone at Balme.[7] These lateral deformations are small, and necessitate the use of very sensitive instruments. Coker

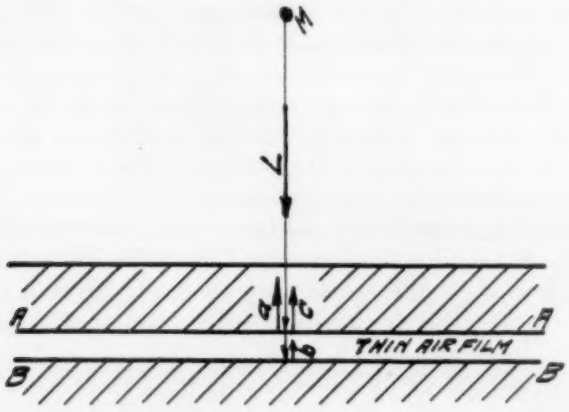
[5] For an application of this method see "A Treatise on Photo-elasticity," by Coker and Filon, 1931, pages 411, 414, or author's paper on "Recent Advances in Photo-elasticity," *Transactions A. S. M. E.*, Vol. 53–11, Sept.-Dec., 1931.

[6] "Mesure des efforts interieurs dans les solides et applications," Buda-Pesth Congress of the International Association for Testing Materials, 1901. A. Mesnager.

[7] Annales des Ponts et Chaussees, 16 (1913), 133–186.

developed a lateral extensometer which he uses successfully on celluloid models measuring quantities of the order of 1×10^{-6} inches. Others, including Mesnager, used interferometers to measure the lateral changes in the thickness. Thus Mesnager measured deformations in his glass model with an accuracy of .0001 mm.

FIG. 3.



In all these methods the model is explored point by point before and after loading, and from the data thus obtained $P + Q$ is evaluated at each point, for it is well known that the lateral deformation δ is given by [8]

$$\frac{-\mu}{E}(P + Q)t, \qquad (2)$$

where μ, E and t are respectively Poisson's ratio, the modulus of elasticity and the thickness of the model. The values of $P + Q$ thus determined are subsequently combined with the values of $P - Q$ obtained photo-elastically to yield the principal stresses P and Q at each point.

It is the purpose of this paper to suggest a method and to show preliminary work for the determination of $P + Q$, the sum of the principal stresses, which does away with the point by point exploration of the existing methods, and which gives

[8] See "Strength of Materials," Timoshenko, Part I, page 64.

photographically a stress-pattern of constant $P + Q$ curves for the complete surface of a model exactly analogous to the stress-patterns of $P - Q$ fringes now obtained photo-elastically, and to show how from these two sets of curves the principal stresses can be completely determined.

BRIEF THEORY OF INTERFERENCE FRINGES.

Let us review briefly the theory of the simplest case of interference fringes. Let a ray L from a monochromatic source M be incident normally on the half-mirror $A - A$, which for concreteness we can take as the polished surface of a glass plate. Upon reaching the surface $A - A$ part of the light is reflected upwards and is represented in our figure by vector 'a' and a part is transmitted. This second ray upon reaching the lower surface $B - B$ is also partially reflected and is designated by vector 'b.' Upon reaching surface $A - A$ this latter vector 'b' is again resolved, a part of it denoted by 'c' being transmitted. The rays 'a' and 'c' meet and combine to form a new ray 'd,' the nature of which depends on the thickness t of the air film. If the difference in the optical path is taken as $2t$, and remembering that upon reflection from a denser to a rarer medium the ray is retarded by $\lambda/2$ we get for the condition of interference the well known equation [9]

$$(2t + \lambda/2) = (2n + 1)\frac{\lambda}{2}, \qquad (3)$$

where n is any integer and λ the wave-length of the light, since interference takes place if the rays meet with a phase difference equal to an odd number of half wave-lengths.

Solving for t we get

$$2t = n\lambda, \qquad \text{or} \qquad t = \frac{n\lambda}{2}, \qquad (4)$$

which means that for a beam of parallel rays interference fringes will appear for n equal 0, 1/2, 2/2, 3/2, etc.

It also means that no two fringes could cross and that along any one interference fringe the depth or thickness of the film is constant. If one surface, say, $A - A$ be considered

[9] See texts on optics.

perfectly flat and taken as a datum plane then the interference fringes would represent contours of the surface $B - B$.

If a body in a two-dimensional stress system has initially flat surfaces these surfaces will after deformation no longer be flat. They will be deformed. If one of these surfaces be polished and a plate of glass with a good optical surface, a datum plane, be brought in contact with it the two planes would be separated by a thin film of air, whose thickness at each point would depend on the stresses at the point. If the face of the model be illuminated by a normal beam of monochromatic light as shown in Fig. 7 the interference fringes thus obtained would be paths of constant thickness of the air film between the datum plane and the face of the model. That the lateral deformations can be revealed by interference fringes has been pointed out by A. Cornu in 1869, who suggested the use of such fringes for the determination of Poisson's ratio.[10]

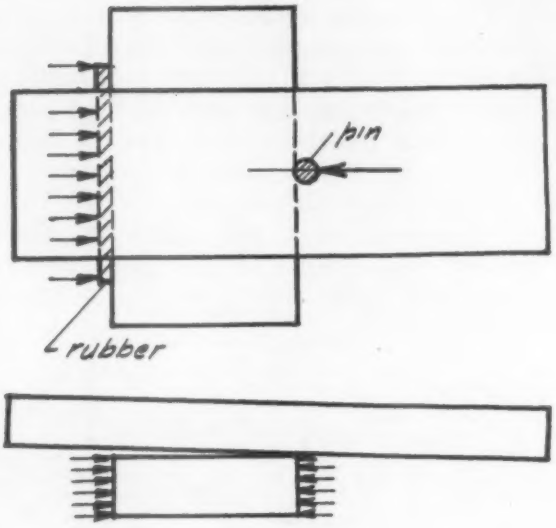
The author wishes to emphasize that if we assume the faces of the model and that of the datum plane before straining to be parallel optical surfaces so that the air film is of uniform thickness, and if we further assume that during the application of the loads to the model the positions of the model and that of the datum plane remain unchanged relative to one another so that the changes in the thickness of the air film could be attributed to the stresses alone *then each interference fringe would directly represent a path of constant* $P + Q$, *which we shall hereafter refer to as a K line.*

After obtaining a qualitative corroboration of the assumption that the interference fringes are affected by the stress system tests were started to obtain an approximate quantitative check. To this end a rectangular glass plate was subjected to a concentrated load along one edge and the other was supported against rubber as shown in Fig. 4.

The choice of this model and loading was prompted by the fact that an exact mathematical solution for the stress distribution exists for an infinite plate subjected to a concentrated load, and because in a small region surrounding the load even our finite and small model could be expected to yield results approximating those of an infinite plate, and thereby provide a first test for our theory.

[10] A. Cornu, C. R., Vol. 69, page 333, Paris, 1869.

FIG. 4.



APPARATUS.

The main equipment used in these tests was:

(1) A monochromatic source of light,
(2) A suitable lens to produce a parallel beam of light,
(3) A straining frame,
(4) A datum plane, and
(5) A camera.

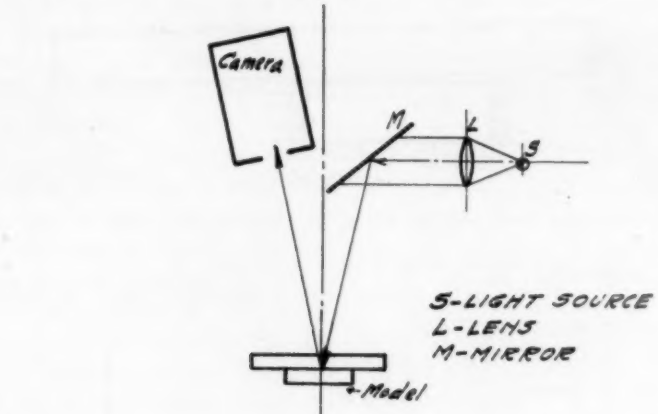
The light source was a mercury-vapor lamp from the photo-elastic apparatus. The camera and lens were similarly from the same set-up. In the preliminary experiments a small vise was used as a straining frame. This, however, is an unsatisfactory arrangement. A good straining frame must satisfy several essential requirements:

(*a*) Adjustments must be provided to keep the pins through which the loads are applied close to the optical surface of the model, and yet not to interfere with the datum plane,
(*b*) The loads must be capable of gradual application,
(*c*) Means must be provided for measuring the loads,
(*d*) Provision must be made to fix the datum plane in space,
(*e*) The loads must be parallel.

A fixture has been designed which we believe will satisfactorily meet the essential requirements mentioned above.

Several optical arrangements have been tried and some are shown in Figs. 5, 6 and 7. To avoid difficulties due to gravity it was found desirable to keep the models and datum plane in a horizontal position. Two types of datum planes were used: plate glass of the windshield variety, and plates having an optical surface with an accuracy of $\lambda/10$. It may, perhaps, be possible to place the model and the straining frame in a basin containing a suitable fluid, to form a thin liquid film over the surface of the model and to utilize this as a datum plane.

FIG. 5.



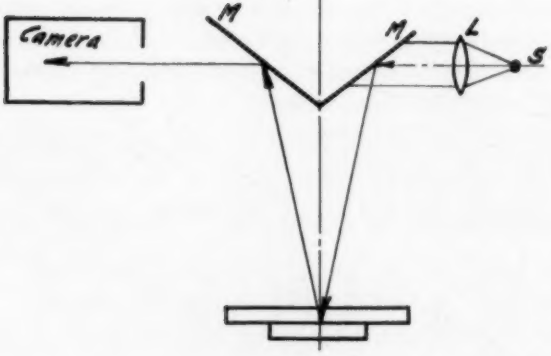


FIG. 6.

FIG. 7.

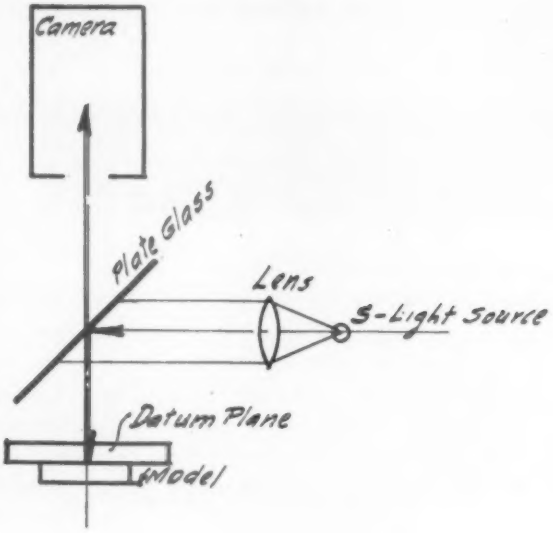
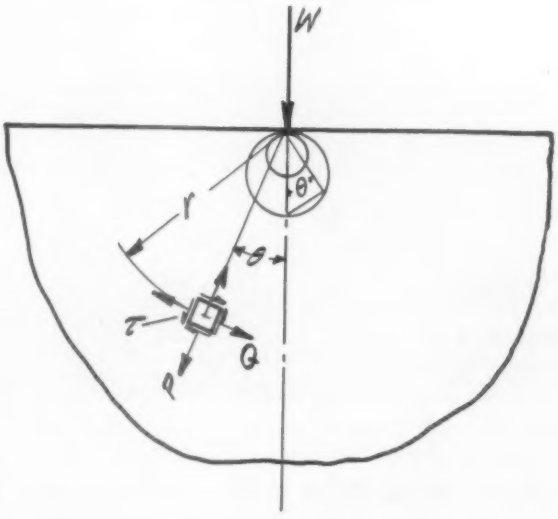

Camera
Plate Glass
Lens
S-Light Source
Datum Plane
Model

FIG. 8.


W
θ
r
s
τ
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p

ANALYSIS OF RESULTS.

The stress function for the case of a concentrated load on an infinite plate is [11]

$$\phi = \mathrm{Ar}\ \theta\ \mathrm{Sin}\ \theta. \tag{5}$$

It can be shown that this function satisfies the continuity equation

$$\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2} + \frac{1}{r}\frac{\partial}{\partial r}\right)^2 \phi = 0 \tag{6}$$

as well as the boundary conditions.

The stresses are given by the Airy functions and reduce to

$$P = -\frac{2W}{\pi}\frac{\mathrm{Cos}\ \theta}{r}, \tag{7}$$

$$Q = \tau = 0, \tag{8}$$

or

$$P + Q = -\frac{2W}{\pi}\frac{\mathrm{Cos}\ \theta}{r}. \tag{9}$$

Putting $P + Q$ equal to a constant C we obtain

$$\frac{\mathrm{Cos}\ \theta}{r} = -\frac{\pi C}{2W} \tag{10}$$

or

$$\frac{\mathrm{Cos}\ \theta}{r} = C_1 \quad \text{another constant.} \tag{11}$$

It will be seen that equation (11) represents a circle with center on the line of the load and diameter d equal to the reciprocal of C_1 or

$$d = \frac{1}{C_1},$$

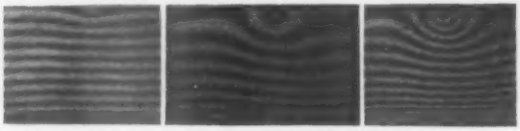
as shown in Fig. 8.

We thus have a simple way of verifying the interference fringe theory as applied to elasticity. If the datum plane touches the edge of the strained model on which the pin is acting then the thickness of the air film in the region immediately surrounding the pin can be neglected and the interference fringes should under gradual application of the load

[11] See "The Mathematical Theory of Elasticity," by A. E. H. Love, second edition, page 208.

and proper illumination change into circles in that region. This is shown in Figs. 9, 10 and 11.

FIG. 9. FIG. 10. FIG. 11.

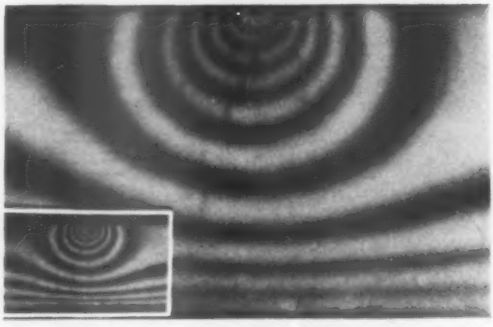


Very small load. Larger load. Largest load.

These figures show changes in interference fringes due to deformations at right angles to the plane of the loads. These photographs were among the first made. In addition to illustrating the effect of the stresses upon the shape of the interference fringes they show, when compared with later work, the progress in the technique of obtaining interference fringe photographs. The optical arrangement for these pictures was as shown in Fig. 5.

The experiment was repeated with a small model having an optical surface of higher accuracy and the results are shown in Fig. 12. The datum plane was, however, unchanged, it still being an ordinary piece of plate glass.

FIG. 12.



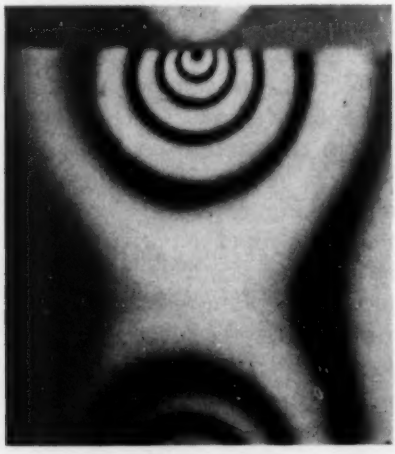
Loading same as in Fig. 4. Insert in lower left corner represents an approximate full size photograph of model.

Special attention is called to the circular dot next to the pin. It can be seen that this dot is tangent to the edge on

which the load is acting as predicted by the stress system from equation (11).

The plate glass datum plane was then replaced by one having a good optical surface of an accuracy of about $\lambda/10$, and the experiment repeated. The resulting interference fringe stress-pattern is shown in Fig. 13. The duraluminum pins through which the loads were applied were $3/16''$ in diameter. Here, again, one can clearly see the circular dot next to the pin through which the load is acting.

FIG. 13.



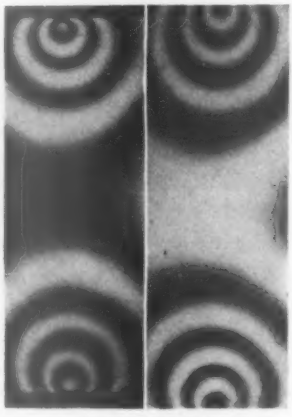
The duraluminum pins were subsequently replaced by $3/32''$ in diameter soft copper pins and the loads applied on opposite sides of the model. Figures 14 and 15 show the resulting interference fringes under slightly different loads.

The circular character of the fringes in the vicinity of the loads is here unmistakably demonstrated and the fundamental assumption of our theory thereby believed to be proved. The fact that the fringes are quite symmetrical about the horizontal and vertical axes may be taken as evidence that they represent the K lines with substantial accuracy.

When the model was under zero the load datum plane was in contact with the model along a fringe containing the

perpendicular bisector to the line joining the pins. Upon application of a small load two black dots appeared next to the pin similar to those shown in Fig. 13, and the previously black fringe at the center cleared up, showing that the region of contact changed from the central line to the circular dots at the pins. Upon application of additional load the circular dots open up into small circles which grow in diameter and move toward the center of the model, other dots appearing to take their place and to follow them.

FIG. 14. FIG. 15.



Smaller load. Larger load.

The fringe order in Fig. 15 was carefully noted and found to be six for the circular dots and three for the fringes nearest the center. The wave-length of the light isolated by the filter from our mercury-vapor lamp is approximately 5460 Å. From this data it is possible to compute the lateral deformation corresponding to each fringe and to construct a complete contour for any cross-section of the model.

Thus far we have considered models and datum planes with accurate optical surfaces and parallel to one another. This, however, is not essential for the determination of the K lines. All that is needed are two fringe photographs and the corresponding loads, such as shown in Figs. 9 and 10. Letting w_1 and w_2 denote two sets of loads corresponding to inter-

ference fringes of order n_1 and n_2 at a point M we have for the lateral deformation δ at a given point corresponding to $(w_1 - w_2)$

$$\begin{aligned} \delta &= 2(n_2\lambda - n_1\lambda)/2 \\ &= (n_2 - n_1)\lambda. \end{aligned} \tag{12}$$

We can thus evaluate δ since the wave-length of the light and the fringe order can be determined. Equating the values of δ from equations (12) and (2) we have

$$(n_2 - n_1)\lambda = -\frac{t\mu}{E}(P + Q), \tag{13}$$

which upon solution gives

$$P + Q = (n_1 - n_2)E/\mu t \tag{14}$$

$$= C_2 \times (n_1 - n_2). \tag{15}$$

If it is desired the constant C_2 can be determined from a compression test from a model of the same material and thickness.

Combining these values with the corresponding values of $P - Q$ we obtain the values of the principal stresses P and Q.

In cases where the interference fringes meet a free boundary the evaluation of $P + Q$ is considerably simplified. Recalling that on a free boundary one of the principal stresses is zero we get for such points the sum of the principal stresses to equal their difference, which difference can be determined photo-elastically. Values of $P + Q$ can be found for two sets of loads w_1 and w_2 and by subtracting obtain $P + Q$ for $(w_2 - w_1)$. The evaluation of P and Q is as before.

The development of photo-elasticity as an engineering tool for stress analysis has been retarded by many factors. The fact that photo-elasticity was limited to transparent materials was undoubtedly responsible for some of the early scepticism. Engineers hesitated to use the results from jellos, glass and even celluloid notwithstanding the mathematical argument that the continuity equation did not contain any elastic constants. It is, therefore, of some significance to point out that the method discussed in this paper *can be effectively carried out with metal models.* Not only can

this be done but it is desirable to do so. Metal models are somewhat cheaper and more practical to handle than glass models. The reason glass was used in the tests described here is that such pieces of glass were readily available.

Further possible applications of the elastic interference-fringe stress-patterns.

Several thoughts suggest themselves in connection with the interpretation of the elastic interference fringes.

They may furnish an additional test for isotropic and singular points, that is for points of equal principal stresses and points of zero stress. At a singular point the $P + Q$ pattern should stay bright under all loads, unless it happens to be a point of contact between the model and the datum plane. At an isotropic point the $P + Q$ pattern would show a fringe whose order would be a function of the loads.

The $P + Q$ stress pattern may also prove of some value for three-dimensional stress problems. That they are capable of showing three-dimensional effects is clearly illustrated in Fig. 16. The model used in most of the tests is shown in Fig. 17.

This model broke during some of the tests into parts roughly indicated by A and B, Fig. 17. Part B was used to obtain photograph of Fig. 16 because it had a good surface and small chamfer. The part to the right of the pins is tapering to zero, and the part to the left is getting thicker. The elastic interference fringes show the effect in these variations in the thickness by distorting the symmetry of the stress-pattern. In order not to confuse the issue only the central portion of this figure was shown in Fig. 15. No claim is here made that these fringes present a solution to the three-dimensional problem. We merely wish to point out that these fringes are affected by the depth of the model.

It might also be possible to apply these fringes to the determination of the formation of plastic regions on any flat surface. It would seem that these fringes should reveal the regions at which a set has been produced. As long as the stresses remain within the elastic limit the removal of the loads should result in a restoration of the initial interference fringe pattern. When the elastic limit is passed no such restoration would seem possible.

The results presented in this paper are essentially of a preliminary character. Further work is now in progress to perfect equipment and technique, to show further agreement

FIG. 16.

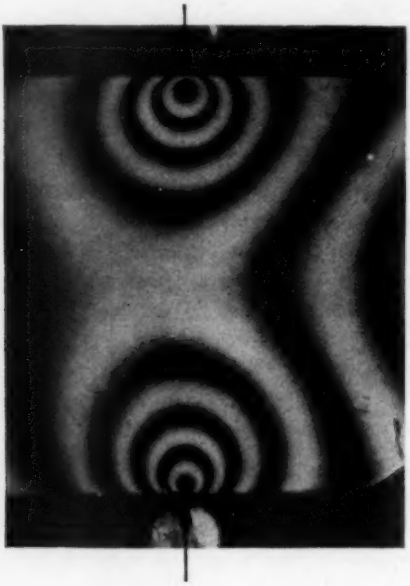
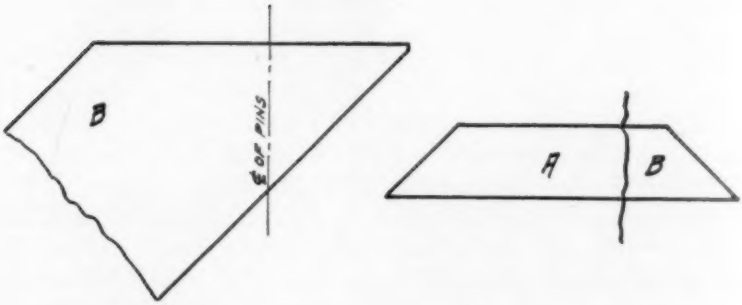


FIG. 17.



between theoretical K lines and the elastic interference-fringe stress-patterns, and to apply this method to new problems.

Acknowledgment is hereby expressed to Mr. H. S. Orr, graduate student in the Department of Mechanics at the Carnegie Institute of Technology for laboratory assistance in connection with this work. The author also wishes to express his appreciation to Dr. Webster N. Jones, Director of the College of Engineering, and to Prof. N. C. Riggs, head of the Mechanics Department, for their interest and support.

December, 1932

Determination of Synthetic Malic Acid in Fruit Products.—Natural malic acid is laevo rotatory and occurs in various fruits. Synthetic malic acid is the racemic form, and is optically inactive. B. G. HARTMANN AND F. HILLIG (*Jour. Asso. Official Agric. Chem.*, 1933, XVI, 277–285) have devised the following method for the detection and quantitative determination of added synthetic malic acid in fruits and fruit products. The total malic acid content is first isolated. Determination is then made of (*a*) total malic acid content by oxidation with potassium permanganate in alkaline solution, and (*b*) laevo malic acid content by the optical method. The synthetic, racemic malic acid content is then obtained by difference.

J. S. H.

Atomic Weight of Arsenic.—GREGORY PAUL BAXTER AND WILLIAM ERNEST SHAEFER (*Jour. Am. Chem. Soc.*, 1933, LV, 1957–1963) have determined the atomic weight of arsenic by comparison of arsenic trichloride with iodine pentoxide. Their results lead to the conclusion that this atomic weight is not far from 74.91. The average value in all the reliable experiments was 74.916. When certain preliminary experiments were omitted, the average was 74.911.

J. S. H.

Atomic Weight of Indium.—GREGORY P. BAXTER AND CHESTER M. ALTER (*Jour. Am. Chem. Soc.*, 1933, LV, 1943–1946) have determined the atomic weight of indium by measurement of the ratio of indium trichloride to silver, and of the ratio of indium tribromide to silver. The mass of silver required to exactly precipitate the halogen present in a given mass of indium trihalide was determined with the aid of the nepholemeter. The value obtained for this atomic weight was 114.76.

J. S. H.

THE AERODYNAMICS OF AN ARROW.

BY

GEORGE JUDSON HIGGINS, B.S. in A.E.

INTRODUCTION.

Archery, though one of the oldest of sports, is relatively new from the viewpoint of the scientist. Years of haphazard experience have decreed certain customs in design and use that have been very firmly rooted. It has remained for a few bold individuals to break away from the customs and approach the game from a scientific basis. The bow has been almost entirely revamped and the arrow is also receiving its share of attention. At the present time, however, not much has been done on the aerodynamics of the arrow. It is the purpose of this article to develop a practical solution to the problem of the aerodynamics of the arrow.

THE DRAG OF AN ARROW.

The resistance of an arrow to motion through the air may be readily determined by a study of its relative motion and the characteristics of resistance or drag on a similar aerodynamic body. Because of the relatively large stabilizing surfaces (feathers) the arrow has far more stability in the air than it requires. This therefore insures that the axis of the shaft will be tangent at all times to its own air path and consequently parallel to its relative wind. Its symmetry will therefore cause the total reaction to the motion to be in the line of the relative wind. This reaction is called the *drag* or resistance.

The drag of a body may be separated into two main divisions, that due to surface (skin) friction of the air particles rubbing over each other and the surface of the body, and that due to the wake or turbulence formed at the rear wherein the airflow is disrupted into the formation of eddies causing energy losses with a corresponding resistance. The exterior shape of the target or flight arrow immediately classifies it as a body

having surface friction drag primarily. If the feathers or vanes are small, straight and well mounted there would be practically no wake. This is very fortunate as it is relatively easy to compute the skin friction drag.

The general formula for surface friction has been developed to the following general form:

$$\text{Drag} = C_D \rho/2\, SV^2 \times \left(\frac{\rho Vl}{\mu}\right)^{-.15} \text{lb.},$$

where C_D = Coefficient of drag,

ρ = Mass density of air, ρ = 0.00238 slug per cubic foot,

S = Area of surface in contact with the moving air, sq. ft.,

V = Relative air velocity, velocity of arrow in feet per sec.,

μ = Coefficient of viscosity of air in $\frac{\text{lb. sec.}}{\text{ft.}^2}$,

l = Characteristic length of surface in feet.

From this it may be seen that the drag varies primarily as the V^2 (velocity squared) and secondarily as $1/V^{.15}$. As the change in velocity of an arrow in flight is not great it will be assumed the resistance varies as V^2 and a suitable C_D will be chosen to make allowance for the secondary variation of $1/V^{.15}$. This is the current practice used in aeronautics.

The surface of an arrow in contact with the air would be that of the shaft and the two sides of the feathers, from which

$$S = \pi dl + 3 \times 2s,$$

where d = diameter of arrow, ft.,

l = length of arrow, ft.,

3 = no. of feathers,

s = area of one side of feather.

This can also be rewritten in the form

$$S = K\pi dl,$$

where K = factor to allow for the additional area of the feathers. (See Table I.)

TABLE I.

Area Factors for Feathers.

$S = K\pi dl.$

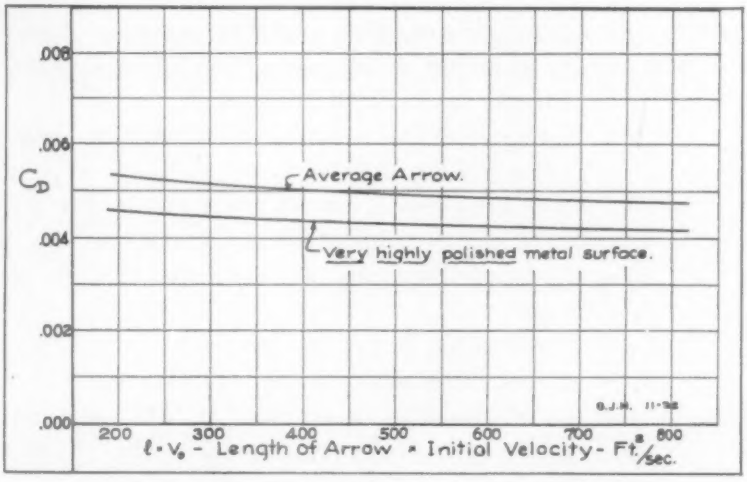
Type of Arrow.	K.
Flight:	
Celluloid vanes	1.02
Feathers	1.03 to 1.05
Target	1.12 to 1.27
Hunting:	
Feathers	1.25 to 1.50
Hunting blades (approx.)	1.20

The expression for drag then becomes

$$D = KC_D\rho/2\ \pi dlV^2.$$

For values of C_D, refer to Fig. 1, wherein C_D values are given for equivalent values of Vl (a form of $\rho Vl/\mu$).

FIG. 1.

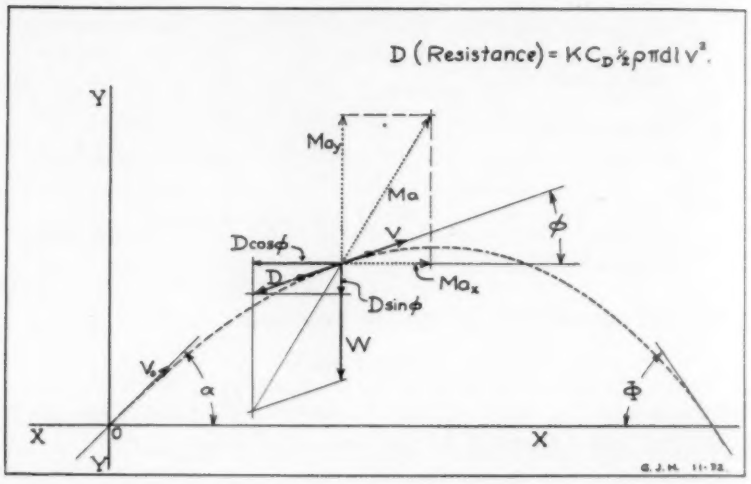


C_D, coefficient of drag (surface friction) for arrows at various velocities.

EQUATIONS OF MOTION.

The equations of motion for the path of the arrow through the air may be set up by reference to the diagram in Fig. 2. A system of axes X–X and Y–Y with an origin at O is established with X parallel to the horizontal.

FIG. 2.



The aerodynamics of an arrow.

Let α = the angle with X at which the arrow is shot, °,

ϕ = the angle of the arrow with X at any subsequent time,

Φ = the angle of the arrow with X when it strikes the ground,

V = the velocity of arrow at any time, ft. per sec.,

V_0 = the initial velocity of arrow, ft. per sec.,

V_x, V_y = the velocities along the respective axes, ft. per sec.,

a = acceleration, ft. per sec. per sec.,

a_x, a_y = accelerations along the respective axes,

g = the acceleration of gravity, 32.16 ft. per sec.^{2},

W = weight of arrow in pounds, $W = Mg$,

M = mass of arrow in slugs,

t = time in seconds.

The force equilibrium diagram is shown in Fig. 2. These forces can be broken up into components along the X and Y axes. This gives the following two equilibrium equations:

$$D \cos \phi = - Ma_x,$$

$$W + D \sin \phi = - Ma_y.$$

Along the X-axis:

$$D \cos \phi = - Ma_x$$

$$a_x = - \frac{D \cos \phi}{M} = - \frac{D}{W} \cos \phi \times g,$$

but

$$D = KC_D \rho / 2 \, \pi dl V^2 = k_1 V^2 = \frac{k_1 V_x^2}{\cos^2 \phi},$$

where

$$k_1 = KC_D \rho / 2 \, \pi dl \left(\frac{\text{lb. sec.}^2}{\text{ft.}^2} \right), \qquad \text{a constant,}$$

$$\frac{d^2}{dt^2} x = a_x = - k_1 V_x^2 \frac{\cos \phi \times g}{\cos^2 \phi \times W} = - \frac{k_1 V_x^2 g}{W \cos \phi}.$$

This expression contains $\cos \phi$, an unknown function varying with V, V_x, and t. Integration for x is therefore very difficult. By means of graphical solutions carried out until the major variations had been deleted, a final set of curves of the "exact" values of a_x, V_x, and x versus time were obtained. See Fig. 3. For the expression

$$a_x = - \frac{k_1 V_x^2 g}{W \cos \phi},$$

the following expression, easily integrable, has been substituted:

$$a_x = 13.5 \frac{k_1 V_0^2 \cos \alpha}{W} t^{0.40} - \frac{k_1 V_0^2 \cos \alpha}{W} g.$$

Let

$$k_2 = \frac{V_0^2 \cos \alpha}{W}.$$

Then

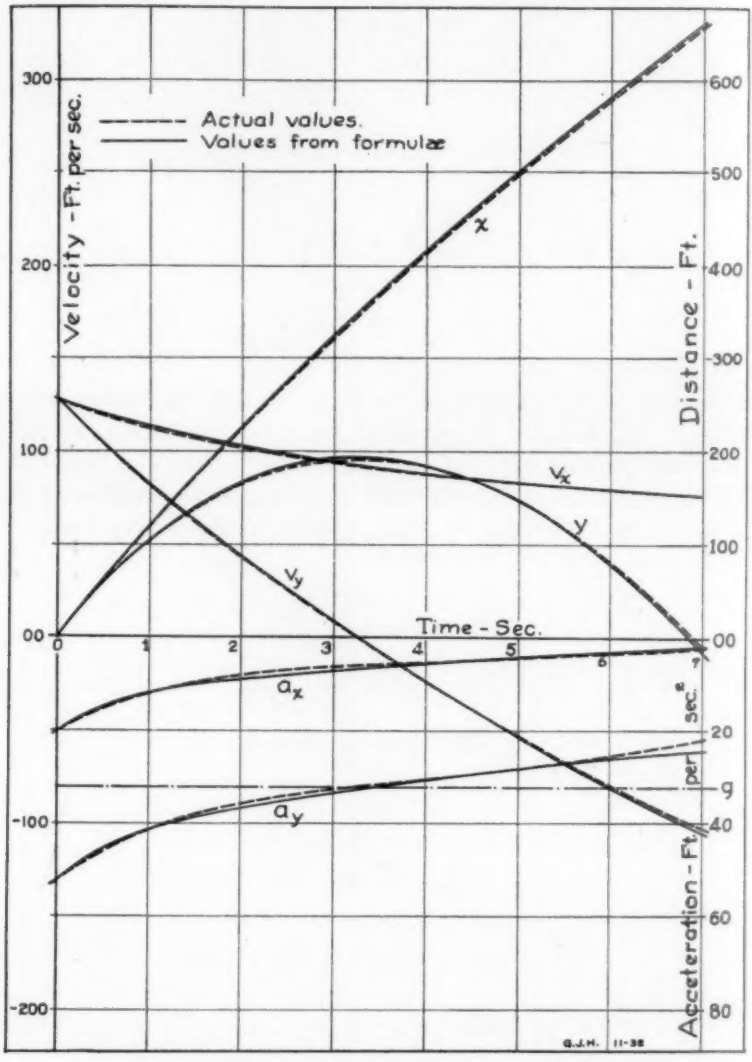
$$\frac{dV_x}{dt} = a_x = 13.5 \, k_1 k_2 t^{0.40} - k_1 k_2 g.$$

Integrating,

$$\frac{dx}{dt} = V_x = 9.64 \, k_1 k_2 t^{1.40} - k_1 k_2 g t + V_0 \cos \alpha,$$

$$x = 4.01 \, k_1 k_2 t^{2.40} - k_1 k_2 \frac{g}{2} t^2 + V_0 t \cos \alpha,$$

FIG. 3.



Comparison of actual values with those from the substitution formulæ.

or completely,

$$x = 4.01\, KC_D\rho/2\, \pi dl V_0^2 \frac{\cos\alpha}{W} t^{2.40} - KC_D\rho/2\, \pi dl V_0^2 \frac{\cos\alpha}{W}\frac{g}{2}t^2 + V_0 t\cos\alpha.$$

Along the Y-axis:

$$W + D\sin\phi = -Ma_y,$$

$$a_y = -\left[\frac{D}{W}\sin\phi + 1\right]\times g;$$

but

$$D = KC_D\rho/2\, \pi dl V^2 = k_1 V^2 = \frac{k_1 V_y^2}{\sin^2\phi},$$

$$a_y = -\left[\frac{k_1 V_y^2}{W\sin\phi} + 1\right]\times g.$$

As for the expressions for x, those for y are also very difficult to integrate as $\sin\phi$ is an unknown variable, a function of V, V_y, and t. In the same manner as above a substitute expression was determined, integrable and comparable to the "exact" curve of a_y; see Fig. 3. The substitute expression is:

$$a_y = (22.5 - .0256\, V_0)k_1 V_0^2 \frac{\sin\alpha}{W} t^{0.482} - \left[k_1 V_0^2 \frac{\sin\alpha}{W} + 1\right]g.$$

Let

$$k_3 = V_0^2 \frac{\sin\alpha}{W}.$$

Then

$$\frac{dV_y}{dt} = a_y = (22.5 - .0256\, V_0)k_1 k_3 t^{0.482} - [k_1 k_3 + 1]g.$$

Integrating,

$$\frac{dy}{dt} = V_y = (15.17 - .0173\, V_0)k_1 k_3 t^{1.482} - [k_1 k_3 + 1]gt + V_0\sin\alpha,$$

$$y = (6.10 - .00695\, V_0)k_1 k_3 t^{2.482} - [k_1 k_3 + 1]\frac{g}{2}t^2 + V_0 t\sin\alpha;$$

or completely,

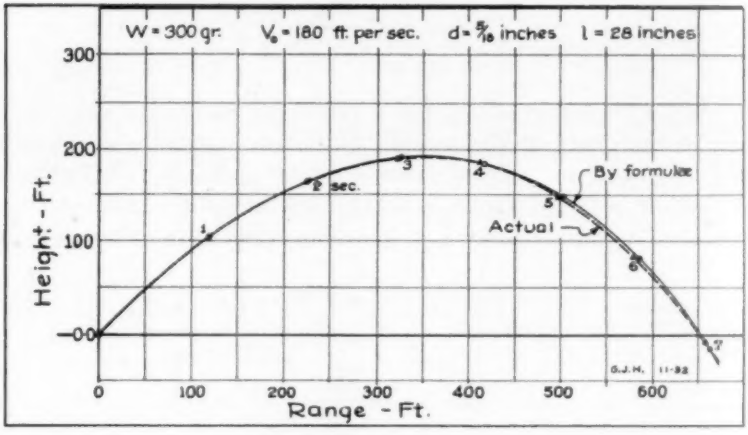
$$y = (6.10 - .00695\ V_0)\ KC_D\rho/2\ \pi dl V_0^2 \frac{\sin \alpha}{W} t^{2.482}$$

$$- \left[KC_D\rho/2\ \pi dl V_0^2 \frac{\sin \alpha}{W} + 1 \right] \frac{g}{2} t^2 + V_0 t \sin \alpha.$$

From the above expressions for x, y, V_x, V_y, etc., the aerodynamical path of an arrow is completely determined.

The accuracy of the above substitution on the final results may be seen in the curves drawn for comparison in Figs. 3 and 4. The "exact" values are given as dotted curves and

FIG. 4.



Flight path of an arrow.

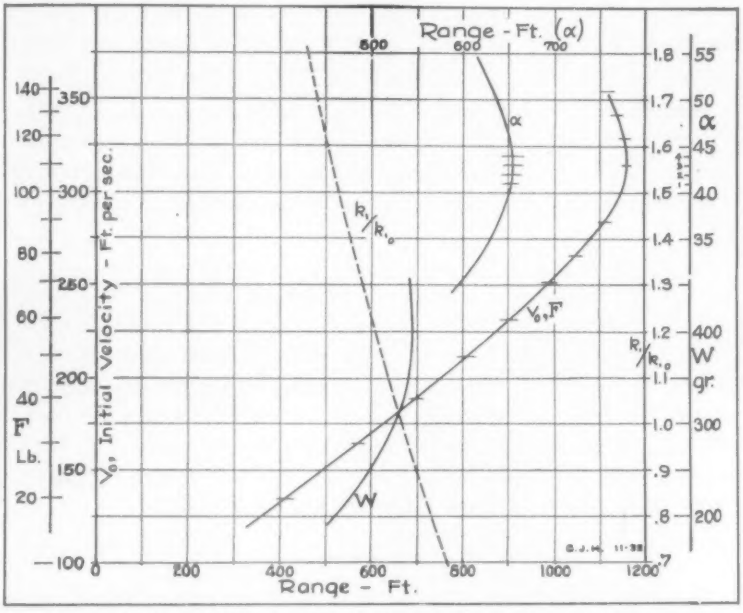
the curves from the formulæ are solid lines. The deviation is not great at any place and the agreement at full range (X) is to be noted. It will be shown later that the maximum deviation is less than the personal deviation of shooting in such a manner that V_0, the initial velocity, is the same.

THE EFFECT OF VARIABLES.

The effect of the change in the values of the variables on the flight path of an arrow has been computed using the above approximate formulæ. An average arrow of 300 grains weight, initial velocity of 180 ft. per sec., 5/16 inch diameter,

28 inches in length, and fitted with flight feathers ($K = 1.05$) was chosen. Times of full range flight and the corresponding ranges were determined. See Fig. 5.

FIG. 5.



Curves showing the effect of a change in the variables—F, V_0, W, K_1/K_{10}, and α.

Angle of Arrow When Shot.—The shooting angle of the arrow is not very important. A value of approximately 43 to 44 deg. gives the greatest range, though a variation of 10 deg. in either direction produces a loss of only about 30 feet, about 4.5 per cent. of the total range.

Effect of K, C_D, d, l.—These factors go to make up the constant k_1. A value for k_1 was chosen as basic, k_{1_0} and fractional increases termed in the ratio k_1/k_{1_0} are given.

$$k_{1_0} = KC_D\rho/2\,\pi dl$$
$$= 1.00 \times .005 \times \rho/2\,\pi \times .026 \times 2.33$$
$$= 0.0000011\,33 \frac{\text{lb. sec.}^2}{\text{ft.}^2}.$$

A ten per cent. change in any one of the factors making up k_1 (K, C_D, d, l) indicates an increase or decrease of approximately 30 feet (4.5%) in the same direction.

Effect of Weight.—The weight of the arrow effects the efficiency of the bow as a unit, increasing the initial velocity (Ref. 1). This fact was considered in computing the changes due to weight. The curve of Fig. 5 shows increased weight is an advantage for greater range, but it can be carried too far apparently as the curve doubles back.

Effect of Initial Velocity and Bow Force.—An increase in V_0 gives an increase in the range obtained. The bow force (F) determines the initial velocity by the following formula:

$$V_0^2 = \frac{l\eta g}{W} F,$$

where η = the efficiency of the bow. Consequently it will vary somewhat similarly to V_0^2. For the computations η was chosen as 0.60. A change of V_0 of five feet per second, a possible variation in shooting, indicates a variation in the range of 26 ft. (4%), which is many times greater than the errors introduced by the substitution formulæ.

GENERAL.

Results from these expressions of short range shots, flight shots, etc., check very well with all available data (Ref. 2 and other tests). The average arrow of 300 grains weight chosen above has a maximum range of 652 ft., taking 6.87 sec. to reach the ground. With an initial velocity of 180 feet per sec. it strikes the ground at a terminal velocity of 127 feet per sec. at an angle of Φ to the ground of 53 degrees. Shot straight up it would reach a peak of 374.3 feet in 4.7 sec. and would return to earth in 10.7 sec. Without resistance its range would have been 1,007 feet and would have shot 504 feet vertically up in the air and returned in 11.2 sec.

CONCLUSION.

The solution of the problem of the aerodynamics of an arrow at best is complicated and the formulæ given in this paper are offered as a possible practical solution of it. It has made

possible computations showing the effects of the different variables which up to the present have only been assumed.

November 23, 1932.

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1. Velocity and Acceleration of Arrows, by C. N. Hickman, Ph.D. JOURNAL OF THE FRANKLIN INSTITUTE, Vol. 208, No. 4, Oct. 1929.
2. The Exterior Ballistics of an Arrow, by F. L. English. JOURNAL OF THE FRANKLIN INSTITUTE, Dec. 1930.

Scientific Cooking of Eggs.—(U. S. Dept. of Agric. Clip Sheet No. 776.) Most people believe the proper way to cook an egg is simplicity itself. Usually the egg is suddenly brought into contact with a hot medium (boiling water or sizzling fat) and removed as soon as it has undergone the desired degree of cooking. The Bureau of Home Economics claims that such a procedure is not at all correct. In the interest of conserving food values it points out that intense heat quickly sets the protein of the egg and makes it hard and leathery. Moderate heat gradually coagulates the protein but leaves it tender and soft.

For "soft-boiled" eggs, place them in cold water, preferably with a rack in the saucepan to keep the eggs from direct contact with the heat. Heat the water gradually to simmering, but do not let it boil. Remove the pan from the fire when the water simmers, cover, and let stand for a few minutes, depending on how well cooked you wish your eggs. For "hard-boiled" eggs in which the whites are tender and the shells do not crack, put them on in cold water, bring them slowly to the simmering point, and keep them at this moderate temperature for about half an hour.

To properly poach an egg, break it into boiling salted water deep enough to submerge it completely, remove pan from the fire, cover, and in about 5 minutes the egg will be ready to lift out on a perfcrated spoon. Such an egg will have a white tender protein yet firm enough to stand up well around the yolk.

The scrambling of eggs should be done in a double boiler. When baking them or making a custard, put the dish in a pan of water and have oven heat moderate (350° F.). . . . Apparently eggs fried are a violation of the principles governing proper cooking and despite their marvelous flavor must be foregone in the interest of "conserving food value of eggs."

C.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

STREAMLINING AUTOMOBILES.

When an automobile is driven along a level road, the power developed by the burning of the fuel is used in part to overcome the friction of the gears and bearings and of the tires on the road. The remainder of the power is used to overcome the resistance of the air. At speeds of 35 or 40 miles per hour the resistance to motion is about evenly divided between rolling resistance and air resistance. At higher speeds the air resistance preponderates and the maximum speed for a given power available is determined by the air resistance.

The power expended in overcoming air resistance appears first as the energy of a wind set up by the passage of the car. Everyone has had the experience of stepping behind a moving car and feeling the strong wind or of seeing the dust clouds stirred up on a dusty road which evidence the motion of the air. These air currents finally die out because of friction in the air and the energy finally appears as heat energy in the atmosphere.

The least possible air resistance would be obtained if there were no air currents set up behind the car and there remained only the friction of the air moving past the surface of the car. The resistance in this case would be less than one-tenth that actually present in a typical modern automobile. It is not feasible to reduce the resistance of an actual automobile to this amount for practical reasons, but considerable improvement can be made.

The large resistance in excess of pure frictional resistance is associated with the setting up of air currents by the motion of the car. The earliest attempts at streamlining were based on the idea of dividing the air gently by a conical cap or a wedge on the front of the car. It has since been found that a blunt nose does not produce any excessive resistance. In a certain sense, the air itself builds up into a cap or wedge, not

* Communicated by the Director.

absolutely at rest with respect to the car but of reduced speed. The real difficulty is to have the air close in smoothly behind the car and be left without forward motion. Air will not turn sharp corners and even with moderately curved surfaces it separates from the surface for reasons associated with the surface friction. However, great improvement can be obtained by rounding sharp corners and keeping the curvature as moderate as possible.

Excrescences of various kinds such as headlights, fenders, door handles, etc., also produce air motions representing additional resistance. For any one element, especially if suitably streamlined, the effect may be small but the sum total is large.

The air resistance may be experimentally determined by means of model experiments in a wind tunnel, a device for producing an artificial wind. With suitable arrangements for representing the effect of the ground the air resistance is the same when the model is held at rest and the air moves as when the model moves and the air is at rest.

At the Century of Progress Exposition in Chicago, a small exhibition wind tunnel has been installed by the bureau. In the tunnel are placed two models, one of a conventional car of today, the other of one design of streamline car. For the conventional car the resistance at 100 miles per hour is about 15 pounds per square foot of frontal area; for the streamline car it is only 6 pounds per square foot of frontal area. (In the exhibition set-up the supporting rods contribute additional resistance.)

The question arises as to the meaning of such a reduction of air resistance in the practical operation of automobiles. There are two ways in which the reduction may be used (1) in securing greater economy or (2) in attaining greater speeds.

At 35 or 40 miles per hour, air resistance represents about one-half the total resistance. A saving of 60 per cent. of the air resistance represents a saving of 30 per cent. of the total resistance and hence 30 per cent. of the power. Therefore, about 30 per cent. less fuel need be burned. At lower speeds the saving will be less; at higher speeds it will be greater. Computations by several engineers have shown that savings of 25 to 40 per cent. may be expected when all factors are included.

Since less power is used in overcoming air resistance, there would be more power available at any speed for acceleration or hill climbing and hence the activity of the car would be improved.

One difficulty, however, arises with this use of streamlining. Since the air resistance is reduced, the maximum speed is increased. However, the gearing between the engine and rear axle is adjusted so that the engine is running at its rated speed and delivering maximum power at the present maximum speed of the car. If the car goes faster, the engine must go faster. This would result in excessive engine speeds, a falling off in the power available, and possible damage to the engine. Hence it would not be possible to open the throttle wide on a smooth level road without damage to the engine.

The obvious remedy is to change the gear ratio to allow the engine to turn slower at a given car speed. This must be done if streamlining is to be used to obtain higher maximum speeds, the gearing being selected to obtain the rated engine speed at the new maximum car speed. However, a new difficulty arises, for now the power available at a given car speed is reduced. Less power is available for acceleration and hill climbing. The activity of the car is reduced; gears must be changed oftener. If a completely automatic transmission is developed and comes into use, this difficulty will disappear but at present it remains as an obstacle to the use of streamlining for increasing maximum speeds.

The model shown in the Chicago exhibit is suitable only for speeds not exceeding 100 miles per hour. When the speed is greater, other important problems arise. In the first place, the lifting effect of the air flow about the car becomes of sufficient magnitude to interfere with proper traction and breaking. In Major Segrave's *Golden Arrow*, inclined planes were used to produce downward forces at the axles to improve the traction.

The second problem at very high speeds is that of stability. Streamline bodies tend to turn broadside to the relative air motion. Hence side winds produce large moments tending to cause the car to skid. This tendency must be counteracted by the use of tail fins having the same function as the vane of

a weathercock. Unlike the weathercock, the surface must be adjusted until the stability is neutral, for it would be just as disastrous to have the car turn into every side wind. Major Segrave determined the proper amount of tail surface by wind tunnel tests.

At low speeds, the lifting and turning effects are present, but their magnitude is small. In one streamline car (Sir Dennistoun Burney's) the lift was estimated to be 300 pounds at 100 miles per hour and only 109 pounds at 60 miles per hour.

The possibility of improved fuel economy or higher speed through streamlining has been known to technical experts for at least ten years and several experimental models have been constructed, especially in Europe. None of these cars has been commercially successful, and the so-called streamlining of present day cars is essentially only a talking point. Some reduction of air resistance has been achieved by rounding corners and other minor changes, but the accomplishments are trivial in comparison with the reduction that is easily possible. The reason for the delay in introducing truly streamline cars lies in the repugnance of the public to radical changes in appearance. No manufacturer has been willing to hazard large sums of money on a car which will not be bought, and attempts are being made to make a gradual transition to cars which are really streamlined.

It is not maintained that the model used in the Chicago exhibit represents the car of the future. Sufficient wind tunnel studies have not been made to exhaust the possible methods of reducing the air resistance. In addition, many problems of a practical nature, for example, improving the accessibility of the engine, must be solved before such a car could be placed on the market. When, however, the public becomes conscious of the advantages of true streamlining and, in sufficient numbers, demands these advantages, manufacturers can and will produce them.

A more technical analysis of this problem will be published in the August number of the *Bureau of Standards Journal of Research*. Separate copies of the paper will not be available till some time after the appearance of the JOURNAL. The Research Paper number and price will be announced in the usual way in this Bulletin.

ENCYCLOPEDIA OF SPECIFICATIONS FOR METALS AND METAL PRODUCTS.

All producers, distributors and large users of metals, alloys, and metal products, will be interested in the new encyclopedia of specifications for metals and metal products which has just been issued by the bureau.

This is a book of about 1,350 pages containing the standards and specifications in this field prepared by more than 80 nationally-recognized organizations authorized to speak for industry or the Federal Government as a whole. All available nationally-recognized specifications embraced within the numerical classification 600 to 699 in the bureau's directory of commodity specifications (Miscellaneous Publication No. 130) are reproduced in convenient form with an adequate index, so that specifications covering any given commodity can be easily located. There are ten chapters covering: Iron and steel; iron and steel manufactures; ferro-alloying ores, metals, and metal manufactures; aluminum, antimony, bismuth, cadmium, and cobalt; copper, brass, and bronze; lead, mercury, and nickel; precious metals, metal jewelry, and plated ware; clocks, watches, and dials; tin and zinc; and miscellaneous ores, metals, alloys, and metal manufactures.

Included in the volume are over 1,600 standards and specifications, given either in full or by suitable abstract, tabulation, or cross reference; descriptions of methods of testing, chemical analyses, metallic coatings, and heat treatment; 1,100 illustrations to supplement the text; 2,000 cross references to demonstrate the close relationship among the specifications assigned to the metals; condensed information in the form of 1,700 tables; and a list of technical societies, trade associations, and other organizations issuing standards and specifications, with addresses to indicate proper sources for information on possible revisions or supplemental data.

This is the third of these encyclopedias prepared by the bureau. The other two cover specifications in the wood-using industries, and specifications for non-metallic minerals and their products. All are companion volumes to the directory of specifications, before mentioned.

Copies of the new encyclopedia, bound in green buckram, entitled "Standards and Specifications for Metals and Metal

Products," Bureau of Standards Miscellaneous Publication No. 120, may be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C., at $3.00 each, post paid in the United States. The price to foreign countries is $4.00.

EFFECT OF VULCANIZATION ON THE REFRACTIVE INDEX OF RUBBER.

Recent measurements of the refractive index of purified rubber vulcanized with different percentages of sulphur indicate that the refractive index increases with the proportion of sulphur combined with the rubber.

The determinations of refractive index were made at approximately 25° C. on a calibrated Abbe refractometer. The method of total reflection instead of grazing incidence was used.

The rubber used for the preparation of samples was free from protein and resins and contained about 99.5 per cent. of the pure rubber hydrocarbon. The samples were vulcanized for a time sufficiently long to bring practically all the sulphur into combination with the rubber.

Results are given here for compounds containing 12 per cent. of sulphur and less. Some measurements were made on compounds containing higher percentages of sulphur, but on account of uncertainties arising from difficulties in making observations further work must be done before these are reported.

Refractive Index of Rubber-Sulphur Compounds.

Sulphur Combined with Rubber.		Refractive Index for D Line at 25° C.	
Percentage by Weight.	Atoms of Sulphur per (C_5H_8) Group.	Observed.	Calculated by Empirical Equation.
0	0	1.5194	1.5190
2	0.043	1.5255	1.5258
4	.089	1.5327	1.5330
6	.136	1.5403	1.5405
8	.185	1.5483	1.5482
10	.237	1.5555	1.5564
12	.290	1.5659	1.5648

The proportion of sulphur is shown in the table both as percentage by weight and as atoms of sulphur for each isoprene

residue or (C_5H_8) group in the rubber. When the refractive index is plotted as a function of the atomic fraction of sulphur, the relation appears to be linear within the probable experimental error. An empirical equation for this relation is

$$n_D^{25^\circ} = 1.5190 + 0.158\ S,$$

where $n_D^{25^\circ}$ is the refractive index of a rubber-sulphur compound measured with sodium light at 25° C. and S is the atomic fraction of sulphur per (C_5H_8) of the rubber. This equation agrees with observations with a maximum deviation of 0.0011 and an average deviation of ± 0.0005.

TEXTILE TEST METHODS.

The proposed revision of Federal Specification No. 345a, to be known as Federal Specification No. CCC-T-191, "Textile Test Methods," which has been under consideration by the textiles committee of the Federal Specifications Board for over a year, has been further revised. It was approved for promulgation by the Federal Specifications Board on May 2. This specification contains the general test methods for textiles purchased by the Government. It is expected that copies will be available from the Superintendent of Documents in the near future.

QUALITATIVE AND QUANTITATIVE ANALYSIS OF TEXTILE MATERIALS.

A key for the identification of textile fibers, including brush and cordage fibers in addition to the fibers used in fabrics, and a method for the quantitative analysis of mixtures containing two or more of the fibers, cellulose acetate rayon, regenerated cellulose rayon, cotton, silk, and wool were prepared and submitted to the textiles committee, D-13, of the American Society for Testing Materials. These methods are being used as the basis for discussion in the development of standard methods for the qualitative and quantitative analysis of textile materials.

The textile section of the Bureau of Standards will furnish mimeographed copies of these methods to anyone interested in submitting constructive suggestions and criticisms.

PROPERTIES OF BUILDING BRICKS.

In a paper by J. W. McBurney and C. E. Lovewell, entitled "Strength, Water Absorption and Resistance to Weathering of Building Brick Produced in the United States," presented at the June 1933 meeting of the American Society for Testing Materials, there is given a rather complete picture of the quality of the brick produced in the United States. Two hundred and fifty-five manufacturers representing 37.4 per cent. of the 1929 brick production submitted a total of 684 samples covering all grades produced. The paper gives weighted averages of several physical properties for both the "hard" and "salmon" brick manufactured in different districts of the United States. The range of strength and water absorption of the brick is given not only for the whole United States but also individually for the principal cities. The grand weighted average for compressive strength of all samples included in the survey is 7,246 lbs./in.^{2} with a range for individual samples of from less than 1,500 to over 21,000 lbs./in.^{2} Water absorption, measured by 5 hour boiling, ranges from less than 2 per cent. up to 34 per cent. with a weighted average for all bricks of 14 per cent.

The paper discusses the question of distinguishing "hard" from "salmon" bricks on the basis of strength and water absorption. The data include the results of 51 cycles of freezing and thawing on approximately 480 specimens, for the most part classified as "salmon," as well as the manufacturers' classification of all samples. It is concluded that no sharp separation of these two grades of brick can be made, but that rejection of salmon grades can be insured by specifying combination of strength or water absorption with values for the ratio of 48 hour cold water absorption to 5 hour boiling water absorption.

DETERMINATION OF SODA IN GLASSES CONTAINING RELATIVELY LARGE AMOUNTS OF POTASH.

A modification of the determination of soda by precipitation as sodium zinc uranyl acetate was reported by Glaze in the *Journal of the American Ceramic Society*, Volume 14, No. 6, 1931, page 450. The presence of large amounts of potash interferes with soda determination by this method. It has

been demonstrated recently that the excess of potash can be removed as perchlorate and the soda determined in the resulting solution.

In the previous work the perchlorates were decomposed before the precipitation of the soda, but it is now evident that it is only necessary to remove the excess perchloric acid by fuming, and the decomposition of the perchlorates is not essential. Consequently, the acid-free sodium and potassium perchlorates are transferred to a weighing bottle, diluted somewhat, and as soon as the insoluble potassium perchlorate has settled out, a weighed portion of the clear supernatant solution is taken for the soda determination. The potash is determined by difference through the combined weights of the sodium and potassium fluosilicates.

Glasses containing from 5 to 20 per cent. soda and from 5 to 30 per cent. potash, analyzed under varying conditions, gave the following percentages of soda: 5.12, 5.12; 5.07, 5.14; 12.55, 12.57; 19.79, 19.78.

GLASS PHASE IN OHIO HEAVY CLAYS.

At the Columbus Station a study is being made of the glass developed in three typical Ohio heavy clays, when heated to vitrification. An alluvial "loess" clay from Zanesville, a shale from Summitville, and a glacial clay from Toledo were selected for this investigation.

The preliminary work was started by making thin sections from samples which had been heated and cooled in the laboratory kilns during the progress of a heavy clay investigation. Powdered samples from the same specimens are also being studied. Briefly, the following was noted:

1. *Alluvial Clay.*—The microscopic examination of this showed a change of color from pale yellow of the raw clay to a deep reddish brown when heated to cone 08. The crystalline character of the clay substance, quartz and mica, was practically unchanged.

In the sample heated to cone 04 a small amount of very heterogeneous highly colored glass was found in the clay substance, cementing together larger mineral grains. The amount of fine-grained crystalline material in the clay substance had decreased.

An increase in the amount of the glass phase and a decrease in the quantity of tiny mineral fragments of the clay substance, continued as samples from specimens heated to cones 3, 4, 6, 7, 8, and 9, were examined. Gas bubbles appeared in the glass of the sample heated to cone 4. Reducing conditions in the kiln enormously increased the solution of mineral grains in the glass phase, accompanied by the production of numerous glass bubbles and the formation of a much clearer, more homogeneous glass phase. In the vitrified samples growth of extremely fine needle-like crystals in the glass phase was noted. These were most abundant near dark iron-rich areas in the glass.

2. *Shale.*—The clay substance in the shale was somewhat similar in appearance to that in the alluvial clay. There was an abundance of plate-like crystalline material and large amounts of limonite. The abundance of opaque aggregates was a distinguishing characteristic of the shales. These aggregates served as a means of differentiating the shales from the other clays. The quartz fragments, though abundant, were finer grained than those in the alluvial clay. The heterogeneous character of the shale was beautifully shown in the thin sections. Some aggregates were made up of fine-grained quartz held together by thin layers of iron-stained material containing little or no mica. Other aggregates were rich in mica and coarse quartz cemented together by heavy layers of brown to black material. Some aggregates were opaque with the exception of a few scattered quartz or mica fragments.

Only a small amount of glass phase was noted in the low fired specimens (cones 08, 06, 04, and 03). It appeared first in the fine-grained clay substance rich in mica and iron oxide. At cone 4 a marked increase in glass was noted. The glass was of a dark color and contained numerous grains of black magnetite and iron rich materials. At cone 7 the glass phase had greatly increased, and the fine crystalline material had disappeared.

3. *Glacial Clay.*—This clay presented a striking difference in appearance from the shale and alluvial clays. Plate-like crystalline material was present in very small quantities in the clay substance, which had a granular appearance. The chief

characteristic of this clay is the presence of large amounts of tiny rhombs of dolomite. A few fragments of feldspar were noted.

The glass phase developed more rapidly in this clay than in the shale and alluvial clays. At as low temperatures as cone 08 appreciable amounts of glass had been developed with a pronounced decrease in the quantity of crystalline material. Practically all of the dolomite had lost its crystalline properties and the grains were etched at points of contact with iron oxide. The amounts of glass phase increased in specimens heated to cones 06 and 04.

At cone 1 very little crystalline material remained. The glass phase, though somewhat clearer, was still far from homogeneous. At cone 3 two changes in the glass phase were the appearance of numerous tiny needle-like crystals and gas bubbles. Small grains of quartz still remained though most of it had been dissolved.

Killing Apple Worms.—(U. S. Dept. of Agric. Clip Sheet No. 776.) The Bureau of Entomology has made available for those who desire them detailed directions on how to prepare chemically treated bands to protect fruit trees against the codling moth caterpillars. These caterpillars start to leave the fruit about the middle of June and seek the nearest dark, protected place for spinning their cocoons. Loose bark on the trunk and branches, or debris on the ground, normally provide suitable quarters. If the trees have been scraped and the orchard thoroughly cleaned up, however, the bands around the trunk of the tree will attract 50 per cent. or more of the worms.

These bands consist essentially of a 2-inch strip of corrugated paper treated with a mixture of beta-naphthol (1 pound) and lubricating oil (1½ pints). Bands so treated, automatically kill practically all the worms that spin their cocoons in contact with it. The number killed may amount to as many as a thousand worms to the tree each season.

C.

Smaller and Better Radios.—(U. S. Dept. of Agric. Clip Sheet No. 777.) The forest service is putting through the final tests a new portable radio set so light and durable that it can readily be carried in the back-pack of a forest worker. It weighs only 13 pounds and will transmit as well as receive voice messages. This set will supplant the older 56-pound portable set designed to receive and transmit both voice and code as well as a smaller portable set weighing 11 pounds which received voice but transmitted code only.

The new set uses short wave-lengths and special new-type tubes, and should be capable of maintaining communication throughout an entire national forest.

C.

THE FRANKLIN INSTITUTE.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting held Wednesday, June 14, 1933.)

HALL OF THE COMMITTEE,
PHILADELPHIA, JUNE 14, 1933.

MR. THEOBALD F. CLARK *in the Chair.*

The following report was presented for final action:

No. 2970: Synchronous Free Pendulum Clock.

This report recommended the award of the Howard N. Potts Medal jointly to F. Hope-Jones and W. H. Shortt, of London, England, "In consideration of their inventive skill shown in the development and the production of a free pendulum type of clock of remarkable precision which is now used to control the standard time in Great Britain and the United States."

The following report was presented for first reading:

No. 2960: Short-Focus Spectrographic Objective.

GEO. A. HOADLEY,
Secretary to Committee.

LIBRARY NOTES.

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BOOK REVIEWS.

THE CATALYTIC OXIDATION OF ORGANIC COMPOUNDS IN THE VAPOR PHASE, by L. F. Marek, Director (Acting) of the Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology, and Dorothy A. Hahn, Ph.D., Professor of Organic Chemistry, Mt. Holyoke College, American Chemical Society Monograph, 486 pages, tables, diagrams, 15.5 × 23.5 cms. New York, The Chemical Catalog Company, Inc., 1932. Price $9.00.

Presumably a review is nearing the stage of perfection when it combines appreciation of an author's work along with fair and unbiased criticism. Offering appreciation is relatively easy compared to the task of making a critical appraisement. The fact that the book deals with a somewhat specialized phase of the very broad and seemingly all-inclusive field of chemistry renders the second obligation of the reviewer doubly difficult to fulfill. Obviously it takes a specialist to catch a specialist and the authors apparently realize it, for, rather than run the risk of embarrassing any itinerant reviewer, they have written a critical summary of their own book. If you doubt that such could be, just read the Preface.

So, with due acknowledgment of such a "break" we now proceed to cover the more attractive feature of our task. To say that the Monographs are getting bigger and better is no exaggeration. The authors can never have possibly heard

about any depression. Really, there never was such a word in the lexicon of chemical research. Chemists may come and go but it goes on forever and the "Catalytic Oxidation of Organic Compounds in the Vapor Phase" is no exception. There are about four hundred and sixty pages closely packed with data, much of which has been tried and tested repeatedly by reliable workers in this field; some are incomplete as to detail since they form the keys to many important industrial processes; and finally, much of the data taken from patents represent more often the enthusiastic claims of the inventors and hence should be taken with a "grain of salt." Of all this, the authors are cognizant and have carefully weighed the data as they go along.

Logically enough, the first chapter plays an introductory role and discusses in a general way the nature and characteristic action of various types of catalysts. In the chapter on the catalytic decomposition of alcohols, it is practically impossible to ignore the dehydration reactions in as much as they are promoted by the same catalysts that bring about dehydrogenation. Whether the loss of hydrogen or of water predominates depends mainly upon the temperature, pressure and other conditions of the reaction rather than any particular specificity of the catalyst. Considerable attention is paid to the oxidation of alcohols to aldehydes using molecular oxygen since this catalytic process is rapidly increasing its importance industrially. Another reaction of promise is that of carbon monoxide with alcohols to form the fatty acids one higher in the homologous series.

When an organic oxidation reaction goes wrong it usually ends with the formation of hydrogen, carbon monoxide, carbon dioxide and water. In other words it has gone too far. But under the proper conditions and over the correct catalyst the desired organic compound can be reformed from these end products. Therefore, in a study of catalysts and equilibrium conditions beneficial to the controlled oxidation of organic materials, a thorough knowledge of the reverse (synthetic) reactions is fully justified. Hence, the chapter on the synthesis of hydrocarbons and alcohols. Some of the basic reactions are that of hydrogen and carbon, carbon monoxide or carbon dioxide to give methane; the decarbonization of carbon monoxide and the catalytic oxidation of carbon monoxide by steam. The methanol process stands out as the typical case of alcohol synthesis and its extensive use has been accompanied by the publication of much reliable data.

The oxidation of methanol to formaldehyde possesses sufficient commercial significance to rate a chapter by itself. Due to the great abundance and availability of raw material, the oxidation of gaseous paraffin hydrocarbons no doubt will become a very important industry of the future. The commercial fuel gases consumed in one year contain around one thousand billion cubic feet of methane and one-sixth as much ethane. A lot of "wood" and "grain" alcohol could be made from these two gases. However, it is not easy to halt the oxidation process at the alcohol stage and until it is, the farmer may rest easy. It would appear for the present that greater promise of obtaining alcohols, aldehydes and ketones lay in oxidizing with oxygen under pressure the higher members of the series—propane, butanes and pentanes.

Although the oxidation of olefins and acetylene has attained little if any commercial development their hydration is of considerable importance. There seems to be no special difficulties attendant to the reaction between ethylene and water to give ethyl alcohol nor acetylene and water to give acetaldehyde. Although the

oxidation of petroleum oils is beset with many difficulties, some excellent pioneering work has been done on an industrial scale. Remember "Aldehol," a particularly obnoxious denaturant of ethyl alcohol. This process may prove the future source of soaps, edible fats and cheaper soapless detergents.

Many synthetic chemical processes require huge quantities of cheap hydrogen and a promising source lies in the partial oxidation of methane possibly direct with oxygen, more probably by using steam. In line with the scope of the book Surface Combustion is allotted a chapter. Particular attention is paid to the several modes of industrial application. As might be expected, the "Cause and Suppression of Knocking in Internal Combustion Engines" is dealt with very fully. The various theories on the mechanism of knock suppression are described and their weak points exposed. About an equal number of explanations on the "Cause of the Knock" also exist. Much interesting data on the effects of the various anti-knock dopes are included in the chapter which is only complete after due discussion of the various theories on anti-knock action.

The oxidation of benzene and its derivatives command special attention since many of the reactions are quite easily controlled and the reaction products enjoy many practical uses, benzaldehyde and benzoic acid especially. In the oxidation of naphthalene we have a cheap source of phthalic anhydride. This process has been highly developed commercially. The oxidation of anthracene to its quinone produces a well-known dye intermediate.

The book concludes with a very useful chapter describing various types of plant scale apparatus adapted to the oxidation of organic compounds. Special attention is given to the problem of heat dissipation from the oxidizing chambers. These may involve high-boiling organic liquids, mercury, lead or fused salt baths. General layouts are given for the production of phthalic anhydride, maleic acid, the oxidation of petroleum oils and the oxidation of methanol to formaldehyde.

T. K. CLEVELAND.

THE STORY OF A BILLION YEARS, by W. O. Hotchkiss, Michigan College of Mining and Technology, 137 pages, maps, 13 × 19 cms. Baltimore, The Williams and Wilkins Company, 1932. Price $1.00.

W. O. Hotchkiss introduces Geology as the easy science. Possibly this was for the benefit of Edith and Nancy to whom the book is dedicated. Possibly it is a concession to the mobs that will visit the great exposition that has been designed to celebrate a Century of Progress. I am reminded of a remark that escaped the lips of a great geologist: "Oh, so-and-so, he is all right. He is a geologist. All geologists are gentlemen." I am very fond of geology and my respect for those who seriously study the secrets of the earth is very great. There are great secrets, as yet unrevealed. I think the author intended to describe geology as the obvious science. Certainly a part of the lure lies in the fact that one can always read a lesson whether confined to the back-yard or privileged to roam at large on foot, by train or by air. There is always the earth below.

The patent illustration of a three-foot canyon guttered by a Michigan storm hands the key to the reader. The key turns as one moves through the book. Beaches and benches tell their story of ancient water ledges; sedimentary and igneous rocks record their origins. The reference to earthquakes and volcanoes left me a little hungry for a more satisfying explanation, especially for the volcano.

It is, of course, an open secret that the last word has not only not been written about volcanoes, but probably the type-caster has not as yet been born who will shape the lead that will print the final page on this dangerous and seductive subtitle of geology—volcanoes and earthquakes.

For a short history of the origin of the earth, its age, the record of life thereon, to be absorbed by a panting patron of the Chicago Fair, I presume that a brief treatment is required. It reminds me a little of the method used to press nourishment into babies who will not eat, to rub them with a superficial application of olive oil. Even the great Ice Age of the Pleistocene which still lingers on Greenland receives bare treatment, an event in the geology of the North American continent without recent rival. It shaped the great lakes and is responsible for the site of Chicago itself. The city fathers can well blow to a heat when they recall the Ice Age and think of the Chicago drainage canal.

Chapter VIII may be most interesting to the casual reader as it tickets the geologic resources we use. Deciduous and all pervasive climate is treated very hastily. The last chapter looks toward the future with longing. The writer is too guarded in expression to startle the Fair with pessimism so he concludes with the pious hope for a better race and "slow progress toward perfection."

HOWARD W. ELKINTON.

CHEMISTRY TRIUMPHANT, THE RISE AND REIGN OF CHEMISTRY IN A CHEMICAL WORLD, by William J. Hale, Ph.D., 151 pages, illustrations, 13 × 19 cms. Baltimore, The Williams and Wilkins Co., 1932. Price $1.00.

It is singularly appropriate that there should be literary support to the exhibition on the shore of Lake Michigan. This book is one of a series that will inform the mind as the splendid and bizarre will inform the eye at Chicago.

Dr. Hale is known to a great many people as director of Organic Chemical Research at the Dow Chemical Company. This, if for no other reason, positions him to speak with convincement about the achievements of the child-science chemistry. It is rather fine that he has dedicated his book to his little daughter Ruth Elizabeth.

The chapters in this readable book of only 151 pages are as so many milestones on the highway of chemistry. If one can start on the threshold of a highway the first chapter squarely plants the reader on the doorstep of time. The threshold is a bit wide, in a strict sense, unless it is necessary to take a running start through Sumeria, Egypt, Judea, with a nod to God en passant, across Greece, scaling Rome, back again to Arabia in order to reach an intellectuo- and physico-genesis in England. The chemico-genesis especially as marked by the development of the synthetic dye industry is assigned to Germany.

It must be very difficult if not impossible to write any book describing the lusty growth of chemistry without plunging into the great war. Dr. Hale submits to this temptation. He redeems the diabolic grimace of chemical warfare by two intriguing chapters "Nature Reveals Herself" and "Chemical Insight Dawns." Immediately upon the heels of this "rosy-fingered" dawn according to the Greeks, came the chemical revolution, a revolution that is still going on in our daily life, before our naked eyes. The rest of the book treats with the influence of chemistry in mining, agriculture and transportation.

One more word about agriculture. The other Sunday I had the good fortune of calling on an old friend—now a farmer in Jersey. On the farm or rather orchard-farm there were no beasts. The horses had been sold and a tractor hauled in their stead. The cows had gone, the pigs had been ground into sausage, the chickens had been reduced to the spit. A stray cat possibly survived by a process of alert escapes. The most important chamber in the barn was the mixing floor. There the fertilizers were prepared. In that "laboratory" the insecticides were ground and compounded. It is the first animal-less farm I have ever been privileged to visit so far in my life. Chemistry was triumphant!

HOWARD W. ELKINTON.

TIME, SPACE AND ATOMS, by Richard T. Cox, Department of Physics, New York University, 154 pages, illustrations, 13 × 19 cms. Baltimore, The Williams and Wilkins Company, 1933. Price $1.00.

The dedication of this book is very illuminating to Time and Space and Atoms if not to Brats.

"*Dear Sir:* You have been with me constantly during the writing of these pages (154). In the approved fashion for those to whom books are dedicated, you have gone over the manuscript with your own hands—and sometimes with your feet . . . for, however physical theories may be transformed from time to time, the behavior of four-year-old brats will doubtless be the same for centuries, and generations of fathers will continue to remain to their offspring, as I now subscribe myself to you,

Your obedient servant,

RICHARD T. COX."

Provincetown, Mass.
August 11, 1932.

All of which throws great light on the book, the whereabouts of the author in August of last year and the whereabouts of the feet upon the pages of the manuscript—but to get down to Time and Space and Atoms. The speed of light, the character of the ether, the four dimensional character of our world all receive serious treatment in a way readily absorbed by a layman prone to lie in a different field. The Chapters on Pulses and Wave-Trains, also Gratings and Spectra, made this subject more clear to me than anything I had previously read. The simple illustrative schematic drawings are particularly illuminating on light. One has a feeling that Mr. Cox will write more on the latter.

The latter part of the book resorts to a description of the atoms and the phenomenon of radio-activity with photons and electrons coming in for their share. The latest on the structure of the atom merits a chapter introduced by a discussion of the quantum theory, a theory which the author modestly and rightly describes as incomplete.

A certain charm lingers after reading the last lines of this book, maybe it is the profoundness of the subject. It may be due to the beaconing of experiment but I think it is largely due to the humanity of the man who signed off to his son as "an obedient servant." To quote the Voices of the Stones and from page 33:

"The suns that rise, the suns that set,
Time's tidal waves of blue and gold
That roll from far ethereal seas,
Hill-land and forest, starlit pool,
Are images we soon forget,
And swiftest when most beautiful.
For when most beautiful we feel
That there is something they reveal,
Some lordlier being of their kind;
And beauty only meaneth this
And to the symbol we are blind."

HOWARD W. ELKINTON.

LABORATORY MANUAL OF PHYSICS, by Clinton Maury Kilby, Ph.D., Professor of Physics in Randolph-Macon Woman's College. 129 pages, 14 × 21.5 cms. New York, D. Van Nostrand Co., Inc., 1930. Price $1.75.

Dr. Kilby has assembled a group of 65 experiments adapted to the needs of elementary college courses. Probably half these experiments are not beyond the resources of high school laboratories and the abilities of high school students, however. The experiments are purposely reduced to their simplest forms both in order to adapt them to as many laboratories as possible and because the author is of the opinion that basic principles may be better inculcated by the use of simple rather than complicated and expensive apparatus. Inevitably a considerable responsibility must be assumed by the instructor who would develop more than the barest principles.

The 65 experiments may be classified about as follows:

Statics and Dynamics	11
Properties of Materials	10
Heat	5
Light	14
Sound	3
Magnetism	2
Electricity	13
Miscellaneous	7

LESLIE R. BACON.

EXPERIMENTAL CHEMISTRY FOR COLLEGES, by J. Allen Harris, M.A., Ph.D., Assistant Professor of Chemistry, University of British Columbia, Vancouver, Canada, and William Ure, M.A.Sc., Ph.D., Assistant Professor of Chemistry, University of British Columbia, 192 pages, diagrams, 20.5 × 26.5 cms. New York and London, McGraw-Hill Book Company, Inc., 1932. Price $1.25.

As a laboratory manual for "first year" college chemistry, this marks a real advance toward the ideal type. Apparently the authors have been untrammeled by any conscious adherence to a particular chemistry textbook and although the assignments number only twenty-two, each one is made to count. Through the

execution of each experiment the student cannot help but acquire considerable knowledge regarding what might be termed as the "key reactions." Such experiments also involve the necessary training in laboratory technique which many manuals attempt to convey separately in one or more preliminary exercises generally meaningless so far as practical chemical application is concerned. The experiments are intentionally constructed in a manner such as will tend to overcome the natural careless and slipshod methods of beginners. This is accomplished by prescribing even a rough weighing out of the reactants in the exercises of qualitative nature and the inclusion of a certain number of procedures that must be conducted in a strictly quantitative manner.

The assignments are logically arranged in three sections. The first deals with the principles of chemistry and includes the determination of: equivalent weights of elements, formulas of compounds by the gravimetric and volumetric methods, molecular weights of gases, molecular weights by the freezing-point method and, rates of chemical reaction. The second section covers the preparation of elements and compounds such as: copper sulfate, cuprous chloride, the double salt-chrome alum, a chlorate and a hypochlorite, sulfur trioxide and its acid by catalysis, nitric and acetic acids from their corresponding salts, high temperature fusions to make permanganates, chromates and dichromates, the preparation of metals by smelting and by the Goldschmidt process. Section three is assigned to the reactions of electrolytes and includes a demonstration of Faraday's law, neutralization controlled through titration, hydrolysis and determination of the equilibrium constant in the formation of complex ions.

All leaves of this book may be detached along a perforated margin and are punched to fit a three-ring loose-leaf note book. Each assignment is furnished with blank page forms on which the student is to write up his results. A page of instructions to students will be found in the front of the manual—an example of the thoroughness of the volume. Practically nothing necessary to the complete guidance of the student has been omitted and any instructor will readily appreciate the relief from responsibility so afforded.

T. K. CLEVELAND.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS.

Report No. 450, The Calculation of Take-off Run, by Walter S. Diehl, 10 pages, diagrams, 23 × 29 cms. Washington, Superintendent of Documents, 1932. Price five cents.

A comparatively simple method of calculating length of take-off run is developed from the assumption of a linear variation in net accelerating force with air speed and it is shown that the error involved is negligible. The run formula is reduced to

$$S = \frac{K_s V_s^2}{\left(\frac{T_1}{W}\right)},$$

where V_s is the take-off speed, T_1 is the initial net accelerating force, W is the gross weight and K_s a coefficient depending only on the ratio of initial to final net accelerating force. Detailed instructions are given for application of the formula and for the calculation of all factors involved.

Report No. 455, Penetration and Duration of Fuel Sprays from a Pump Injection System, by A. M. Rothrock and E. T. Marsh, 10 pages, illustrations, 23 × 29 cms. Washington, Superintendent of Documents, 1933. Price five cents.

High-speed motion pictures were taken of individual fuel sprays from a pump injection system. The changes in the spray-tip penetration with changes in the pump speed, injection-valve opening and closing pressures, discharge-orifice area, injection-tube length and diameter, and pump throttle setting were measured. The pump was used with and without a check valve. The results show that the penetration of the spray tip can be controlled by the dimensions of the injection tube, the area of the discharge orifice, and the injection-valve opening and closing pressures.

PUBLICATIONS RECEIVED.

The Development of Physical Thought, A Survey Course of Modern Physics, by Leonard B. Loeb, and Arthur S. Adams, 648 pages, illustrations, 14.5 × 22.5 cms. New York, John Wiley & Sons, Inc., London, Chapman & Hall, Ltd., 1933. Price $3.75.

Elementary Quantitative Analysis, Theory and Practice, by Hobart H. Willard and N. Howell Furman, 406 pages, tables, illustrations, 14.5 × 22.5 cms. New York, D. Van Nostrand Company, Inc., 1933. Price $3.25.

The Great Enigma, A New View on the Outlook of Life, by Hugo Hermann Schauinsland, translated from the German by Walter H. Schauinsland, 93 pages, 13.5 × 19.5 cms. New York, E. P. Dutton & Co., Inc., 1933. Price $1.25.

Gas Analysis by Measurement of Thermal Conductivity, by H. A. Daynes, 357 pages, tables, illustrations, 14 × 22.5 cms. Cambridge, University Press, 1933. Price $4.25.

Physique Moleculaire Matiere et Energie, par Victor Henri, 429 pages, tables, 16 × 25 cms. Paris, Hermann et Cie., 1933. Price 110 frs.

Les fondements de la théorie de la Relativité Générale, Théorie unitaire de la Gravitation et de l'Electricité, Sur la Structure Cosmologique de l'Espace, par Albert Einstein, traduit de l'allemand par Maurice Solovine, 109 pages, 16.5 × 25 cms. Paris, Hermann et Cie., 1933. Price 35 francs.

The Heroic Age of Science, the Conception, Ideals, and Methods of Science Among the Ancient Greeks, by William Arthur Heidel, 203 pages, 15.5 × 23.5 cms. Baltimore, Williams & Wilkins Co., 1933. Price $2.50.

A Century of Progress Series, Sparks from the Electrode, by C. L. Mantell, 127 pages, illustrations, 13 × 19 cms. Baltimore, Williams & Wilkins Co., 1933 Price $1.00.

Differential Equations for Electrical Engineers, by Philip Franklin, 299 pages, 14 × 22.5 cms. New York, John Wiley & Sons, Inc., London, Chapman & Hall, Ltd., 1933. Price $2.75.

Sir Parfulla Chandra Ray, Seventieth Birth Day Commemoration Volume, 362 pages, 17 × 26 cms. Calcutta, Indian Chemical Society, 1933.

Mémoires sur la Mécanique Ondulatoire, par E. Schrödinger, 234 pages, 16 × 24 cms. Paris, Librairie Felix Alcan. 1933. Price 50 francs.

Die Elektrische Warmbehandlung in der Industrie, von E. Fr. Russ, 259 pages, illustrations, 16.5 × 24 cms. München und Berlin, Verlag Von R. Oldenbourg, 1933.

Canada Department of Mines, Canadian Limestones for Building Purposes, by M. F. Goudge, 196 pages, tables, illustrations, 16.5 × 24.5 cms. Ottawa, King's Printer, 1933. Price thirty cents.

Actualites Scientifiques et Industrielles, No. 63, L'Univers en Expansion, par Henri Mineur, 41 pages, 16.5 × 25.5 cms. 1933. Price 12 francs. No. 68, Réel et Déterminisme dans la Physique Quantique, par Emile Meyerson, 49 pages, 16.5 × 25.5 cms. 1933. Price 10 francs. No. 70, Les Théorèmes de Conservation dans la Théorie des Chocs Électroniques, par L. Goldstein, 26 pages, 16.5 × 25.5 cms. 1933. Price 9 francs. Paris, Hermann et Cie.

National Advisory Committee for Aeronautics, Technical Notes, No. 443, Wind-Tunnel Research Comparing Lateral Control Devices, Particularly at High Angles of Attack. VII, Handley Page Tip and Full-Span Slots with Ailerons and Spoilers, by Fred E. Weick and Carl J. Wenzinger, 20 pages, tables, diagrams, 20 × 26 cms. Washington, Committee, 1933. No. 444, Working Charts for the Stress Analysis of Elliptic Rings, by Walter F. Burke, 6 pages, diagrams, 20 × 26 cms. Washington, Committee, 1933. No. 458, Wind Tunnel Research Comparing Lateral Control Devices, Particularly at High Angles of Attack. XI, Various Floating Tip Ailerons on Both Rectangular and Tapered Wings, by Fred E. Weick and Thomas A. Harris, 19 pages, tables, diagrams, 20 × 26 cms. Washington, Committee, 1933. No. 459, Wind-Tunnel Tests on Model Wing with Fowler Flap and Specially Developed Leading-Edge Slot, by Fred E. Weick and Robert C. Platt, 10 pages, figures, tables, 20 × 26 cms. Washington, Committee, 1933. No. 461, The Effect of Rivet Heads on the Characteristics of a 6 by 36 Foot Clark Y Metal Airfoil, by Clinton H. Dearborn, 6 pages, figures, 20 × 26 cms. Washington, Committee, 1933. No. 462, Formulas for the Stress Analysis of Circular Rings in a Monocoque Fuselage, by Roy A. Miller and Karl D. Wood, 15 pages, tables, figures, 20 × 26 cms. Washington, Committee, 1933. No. 463, Aerodynamic Tests of a Low Aspect Ratio Tapered Wing with Various Flaps, for Use on Tailless Airplanes, by Fred E. Weick and Robert Sanders, 6 pages, figures, 20 × 26 cms. Washington, Committee. 1933.

CURRENT TOPICS.

Natural Resin Origins.—(A. J. GIBSON, *Chem. & Ind.*, 52, 58.)

Copal.—The copals are the resinous exudations mainly from species of Coniferae occurring in East India, East Africa, West Africa and South America. These resins may be classified into hard, medium and soft copals. The quality of copal decreases with increased specific gravity and the property of oil-solubility is imparted by an old established process known as "running" and is the heating of small batches of resin accompanied by a loss in weight and added solubility in oils.

Dammar.—The dammars represent those resins derived from trees belonging to the large tropical tree-family of the Dipterocarps. A peculiarity of the resins is their insolubility in alcohol and their complete solubility in coal-tar hydrocarbons, turpentine and also petroleum hydrocarbons. The trees producing these resins are found in the East Indies, the Malay Peninsula, and the islands of the Pacific generally. De-waxed dammar is also in demand and research has been done to remove its undesirable component the "b-resene."

Kauri.—This resin is both fossil and recent and is obtainable from a species of Arancarineae. Captain Cook mentions kauri in his diary of November, 1769 but it did not achieve commercial importance until three-quarters of a century later. The fossil gum is known, as "range gum" or "swamp gum" while the new resin from tapped trees is known as "bush gum."

Lac.—Most of this resin, about 97 per cent., is produced in India. It is unique in being an animal product, unlike most of the natural resins which are of vegetable origin. Lac is the resinous incrustation of a small-scale insect living on certain trees. This incrustation is a rigid protective armor that causes little or no inconvenience since the insect has no power of mobility throughout the greater part of its life-cycle. The raw material for the resinous crust is sucked from the tree and is converted in what must be the most compact and well-equipped laboratory in the world—for the insect is only 1/32 in. long—into what is known as sticklac, consisting of a water-soluble dye, a compound wax, an alkali-soluble dye, moisture, sugars, soluble salts and the two true lac resins whose constitution is still under investigation. The magnitude of production is such that it is rated in grams per thousand insects, yet the total annual production approximates sixty-five million pounds.

Lac has been known for centuries, but the insect was first described by Father Tachard of the Society of Jesuits, 1709 and was named after him *Tachardia lacca*. The name has altered many times, the latest being *Laccifer lacca*. Sticklac usually is harvested by the natives who strip it off the tree, crush, sieve and wash it, this last process removing the water-soluble dye. Dried in the sun, this forms the seed-lac of commerce. The seed-lac is converted by a primitive heat process into button lac and shellac.

C.

Invention of the Toothbrush.—(*White Metal News Letter.*) The invention of the toothbrush grew out of the famous Gordon Riots of 1780 which took place in London. William Addis the inventor, who was being sought as an alleged participant in the riots, hid in the home of a leather tanner where he amused himself by carving bone, in those days a fashionable art. At that time the cleaning of teeth was a crude operation, the process being carried out by a single twig which was shaped like a chisel, and rubbed over the teeth with an up-and-down motion.

Wanting something better, Addis bored a few holes in a piece of bone, cut some hairs from the tail of the nearest cow hide, thrust these into holes and thus became the maker of the first toothbrush.

Toothbrush handles today are generally made from celluloid. The bristles are mainly obtained from Siberian pigs, the wild species producing the best, having hair which is both long and stiff. Special machines are used to insert the tufts of bristles in the handles, and each tuft is firmly secured by a nickel siver anchor.

C.

Locomotives, Past, Present and Future.—(L. F. LOREE—To the American Members of the Newcomen Society.) The first steam locomotive was operated by Richard Trevithick on Christmas Eve, in 1801. The final supremacy of this method of transportation was established on Oct. 6, 1829, by George Stephonson's engine, the "Rocket" in the competitive trials at Rainhill on the Liverpool and Manchester Railway. The "Rocket's" performance demonstrated the practicability of operating an engine with wheels having smooth rims over smooth steel rails. Even with the large modern locomotive it is seldom realized how small is the area of contact between the wheel and rail. It is about one-third of a square inch for each wheel, a space about as large as one's thumb-nail.

The first locomotive to be operated in the United States was the "Staurbridge Lion" which was put into service on the Delaware and Hudson in 1829. The latest locomotive placed in operation on this

line is the "James Archibald" which has a working capacity just 291 times as great as its century old predecessor. This new locomotive carries 500 pounds steam pressure, weighs 150 tons and exerts a tractive effort of 75,000 pounds, capable of drawing the combined loads of 97,500 pack horses.

The ten years following the successful trial of the "Rocket" in 1829 saw great improvements in design and construction. The cylinders were placed horizontal; the fire-box was built integral with the boilers; the tender was changed from a truck and barrel to the present type; the smoke box was added; but the outstanding improvement was securing in 1839 an exhaust clearance by a lap in the valves, reducing the back cylinder pressure and increasing the use of the expansive properties of the steam. All these improvements made a 70 per cent. reduction in fuel consumption.

Following this approximately ten year period of rapid improvements, changes were introduced from time to time with long intervening periods of quietude. Some of the more significant were: fire-box baffle walls; the compound engine, at first impracticable with the saturated steam, but now again coming into use with the comparatively dry steam created by superheating; the introduction of the piston valves; and the very notable addition of the superheater by Schmidt, since greatly improved.

Further great improvements are still possible. One of the most inviting is to reduce the expense of construction, and especially of maintenance, by reducing the number of parts. The modern locomotive consists of some 15,000 separate and distinct pieces. The substitution of four drawn seamless steel drums for the conventional fabricated type in the new locomotive reduced the number of pieces by 660. The substitution of a welded boiler for the present built-up boiler would reduce the number of pieces by 2492 and the dead weight by 4750 lbs. Many parts can be lightened by molding them from powdered metals rather than casting from molten metal.

The old engine had a thermal efficiency of about 4 per cent. The "James Archibald" has an efficiency of 10½ per cent. while the new locomotive (1403) it is believed will show a thermal efficiency of 14½ per cent. This locomotive is equipped with poppet valves, roller bearings for the main driving axle, a feed water heater putting water into the boiler at 235 degrees, and is a triple expansion engine, the high pressure cylinder carrying steam at 500 pounds, the intermediate at 290 and the two low pressure cylinders at 145 pounds, all working upon the same driving axle.

There is every indication that the thermal efficiency can be increased still more by instituting such improvements as using a waste gas economizer to raise still further the temperature of the

boiler feed water; preheating the air for combustion; adopting a mechanical draft and reducing further the cylinder back pressure. An improved type of superheater would permit raising the present limitation on temperature. Increasing the boiler capacity as well as avoiding the now very undesirable condition of the final passing of the superheated steam through the coldest part of the boiler which removes a substantial portion of the heat that has been so expensively supplied, also gives promise of greater thermal efficiency. All these improvements would increase the possible heat recovery to 18 per cent. Modern power stations develop a thermal efficiency of 25 per cent. at the present time.

C.

Infra-Red Rays Raise Legibility of Egyptian Manuscripts.—(*Chem. & Ind.*, **52**, 459.) An interesting development in infra-red photography in its application to the deciphering of illegible manuscripts has been recently reported. The Museum photographer at the British Museum has been experimenting with early Egyptian texts on leather that have so far been impossible to read. The leather had curled and bubbled into a dark mass on which letters could be seen but too dimly to be deciphered. A fragment about 10 in. by 6 in. was photographed with an infra-red plate and the resulting photograph showed the writing so clearly that it could be read with ease. This fragmentary success encouraged the Museum authorities to have photographed the whole of this particular leather text.

C.

A New Disinfectant.—(U. S. Dept. of Agric. Clip Sheet No. 778.) The Bureau of Animal Husbandry in its search for new and better disinfectants against livestock diseases has discovered that sodium orthophenylphenate is highly effective in destroying tubercle bacilli on premises where tuberculosis is being eradicated. This new germicide has only a slight odor, is readily soluble in water and not severely poisonous to livestock. In using this new disinfectant it is necessary to apply the solution at a temperature of 60° F. or more.

C.

Slag Cement for Dam Construction.—(*Ind. & Eng. Chem.* News Edition, **11**, 147.) Ever so often a letter is received from Scandinavia, telling about the latest chemistry developments in that northern peninsula. The most recent of these letters describes a pioneering step in the construction of concrete dams the outcome of which

will eagerly be watched by engineers the world over. It seems that during recent years flaws have developed in the older of the concrete dams in Norway and other countries, because of water penetrating through the unavoidable pores and fissures in the cement and dissolving away the free lime. In order to reduce or eliminate this attack by water not only a denser type of concrete was desirable but also one containing a high proportion of ingredients insoluble in water. A cement that would not develop too much heat also was advisable as a precaution against the ultimate formation of contraction fissures.

Acting on the advice of several experts and authorities, O. ROLFSEN, construction engineer of the new Groenvollfass dam decided to use a slag cement in its construction. A cement grinding mill was installed at the place of building and sufficient storage capacity provided so as to permit the conduction of three-day laboratory tests. The cement was a ground mixture of 30 to 40 per cent. of first-grade well-burned Norwegian Portland cement clinker and 60 to 70 per cent. of chilled blast furnace slag obtained from Germany. The resulting concrete had a specific gravity of 2.45 and a water absorption power after hardening of 2.2 per cent. Laboratory leaching tests showed that the slag cement had a resistivity against dissolution by water three times greater than that of Portland cement. The heat developed upon hardening by the slag cement was approximately only 50 per cent. of that for regular cement.

Several cement people and construction engineers expressed the opinion that the slag cement would not hold up so well as Portland cement over prolonged periods of time and felt that by correct proportioning of the mixes a concrete practically impervious to water could be obtained with regular cement.

C.

Epidos.—(*Ind. & Eng. Chem.*, News Ed., 11, 148.) Whether this is the word the Greeks had for it, is not known but in this day and age "Epidos" stands for the International Association of Bone Glue Manufacturers. This association has announced an international competition intended to promote the development of uses of bone glue, and with prizes amounting to 20,000 Swiss francs. The judges will consider the results of research for the purpose of using bone glue in the manufacture of new products and those into the composition of which bone glue has not hitherto entered as well as improvements in processes already employing bone glue which will permit the further development of its use. The competition is open to all interested.

C.

Turtle Oil.—(*Drug & Cosmetic Ind.*, 32, 211.) Since turtle oil has risen to a place of importance as a raw material for the manufacture of cosmetics, F. W. BROWN, a chemist in this field, has come forward with some facts pertinent to its newly-found application. The facts are of primary interest to the manufacturer of cosmetics many of them having been taken unawares by the sudden popular demand for products containing this ingredient.

Common commercial turtle oil is obtained chiefly from the loggerhead turtle which is caught and rendered in the tropics and semi-tropical regions. This oil is dark in color and has a strong fishy odor. The oil from the green turtle promises to be the most desirable variety of turtle oil for cosmetic purposes. It is of a strong yellow color and possesses an individual but persistent odor, not particularly fishy when fresh, but develops a fishy odor upon standing exposed to the air. The difference in the odors of the oils may be explained by the fact that the green turtle is a strict vegetarian while the loggerhead turtle is a scavenger.

It is a question whether sufficient green turtle oil will be available to meet the demands of the cosmetics. At present it is a by-product from the canning of green turtle substance and the making of green turtle soup. A four hundred pounder contains about 20 pounds of oil some of which must be retained by the flesh if it is to remain as a popular food item. Apparently there will be no scarcity of loggerhead oil since something like one hundred and ten thousand gallons are used annually on the northeast coast of South America and several thousand gallons are exported annually from the Seychelles to London.

When turtle oils from various sources were incorporated in cosmetic preparations it was found that in the case of cold creams lesser quantities of the waxes and spermaceti were required for a given consistency. Very satisfactory lotions containing turtle oil were prepared using triethanolamine with stearic or oleic acid. The fact that turtle oil contains some vitamin A may or may not be played up in the advertisements of turtle-oil cosmetics.

C.

Notices of Judgment under the Food and Drugs Act.—The Federal Food and Drugs Act was approved June 30, 1906, and became in force and effect from and after January 1, 1907. One clause of the Act provides for the publication of notices of judgment of the court in cases brought under the Act. These notices are issued in serial form by the United States Department of Agriculture, and, at the present time, by its Food and Drug Administration. Notice of Judgment Number 1 was issued May 2, 1908.

The latest Notices issued are dated May, 1933, and are numbered consecutively 19,901 to 20,000, both inclusive. Therefore in the period of slightly less than twenty-six and a half years since the Act became effective, 20,000 cases have been brought under it and its amendments, and have been decided in the courts. Incidentally, a period of twenty-five years has elapsed between the publication of the first and the 20,000th Notice of Judgment.

J. S. H.

Award of the Thomas Burr Osborne Medal to Clyde H. Bailey.—This medal is awarded by The American Association of Cereal Chemists to outstanding leaders in the field of cereal chemistry; it is named in honor of Osborne and his classic studies in the field of the plant proteins, particularly the proteins of the cereals. On May 23, 1932, the medal was presented to Clyde H. Bailey, professor of agricultural biochemistry at the University of Minnesota, who has made numerous researches on milling, baking, grain storage, wheat breeding and cultivation, and related subjects. The proceedings of the presentation are published in a 30 page supplement to *Cereal Chemistry*, volume X, number 3, May, 1933. Dr. Bailey's address on the occasion was entitled "A Quarter Century in Cereal Chemistry." Among the subjects discussed are the proteins, carbohydrates, lipoids, pigments, and enzymes of the cereals, the agents used for bleaching flour, and the applications of hydrogen ion concentration in cereal chemistry.

J. S. H.

Permeability of Membranes to Aluminium Cations.—HENRY KOWALZYK (*Mendel Bulletin*, 1933, V, 68–73) has studied the diffusion of aluminium cations from an aqueous solution of aluminium sulphate through various membranes into distilled water. The membranes used were cellophane, gelatin (filter paper impregnated with gelatin, then hardened by means of formaldehyde), sheet collodion, filter paper impregnated with collodion, large intestine and cecum of sheep, pig intestine, beef intestine. The period of diffusion was at least 1 hour. The aluminium sulphate solution contained 0.1 milligram of that metal per cc. The per cent. of the aluminium which diffused through the membrane was least with the filter paper-collodion membrane (0.520 per cent.), and greatest with the round beef intestine (18.380 per cent.). Speculative and indirect evidence of the absorption of aluminium ions in the animal body was thus obtained.

J. S. H.

Composition of Canning Tomatoes.—L. G. SAYWELL AND W. V. CRUESS (University of California, Coll. of Agriculture, Agric. Exp. Sta., Bull. 545, 32 pages, 1932) find that various conditions may influence the chemical composition of tomatoes. The per cent. of total solids (1) is higher in California tomatoes than in those grown in the eastern United States, (2) becomes lower as the summer temperature increases, (3) is higher in tomatoes from plants suffering from lack of water than in those from well-irrigated plants, and (4) tends to be lowest in tomatoes gathered during November, highest in those gathered during October, and to occupy an intermediate position in those gathered during September. Purchase should be made for manufacturing on the basis of content of total solids. The chemical composition of the tomato varies with the variety, the plant, and the position on the plant. The locules contain more total acids, far less acid-hydrolyzable material, and slightly less total solids, reducing sugars, and protein than the cores and walls. The cores are richest in total solids and reducing sugars. On the average, the tomatoes contain 0.97 per cent. protein, less than 0.05 per cent. sucrose, less than 0.05 per cent. starch, and 0.74 per cent. insoluble solids. Practically all the sugars are reducing sugars. The pectin content varies considerably with the variety, time of picking, degree of ripeness, and locality. A very active invertase is not present. The hydrogen ion concentration of the pulp, expressed as pH, ranges between 3.8 and 4.4, with an average value of 4.1; over two-thirds of the samples had values between 4.0 and 4.2. High titratable acidity was usually accompanied by a low pH value, and vice versa.

J. S. H.

Rôle of Magnesium in Animal Nutrition.—H. D. KRUSE, ELSA R. ORENT, AND E. V. MCCOLLUM (*Jour. Biol. Chem.*, 1933, C, 603–643) have produced a condition known as magnesium tetany in experimental animals by feeding a ration containing only 1.8 parts per million of magnesium, but adequate amounts of other constituents. This condition terminates in death. The magnesium content of the blood serum decreases; and nutritional failure is manifest by changes in the lipins of the blood:—the total fat remains constant; the total cholesterol increases; and the cholesterol esters increase. These changes are evidence of failing fat metabolism, and are entirely dissimilar from those occurring during fasting. The available data do not permit a conclusion as to whether the changes in lipoid metabolism during magnesium deficiency occur also in all other cases of partial inanition. The

tetany and its convulsions are attributed to the decreased magnesium content of the blood serum.

J. S. H.

Freezing Point of Hen's Egg.—H. P. HALE (*Proc. Royal Soc.*, London, 1933, *B*, CXII, 473–479) states that the freezing point of the yolk of the hen's egg may be taken as − 0.57° C., and the freezing point of the white as − 0.42° C. When seeded separately, both the thick white and the thin white have the same freezing point, − 0.42° C. ARTHUR W. THOMAS AND M. IRENE BAILEY (*Ind. Eng. Chem.*, Ind. Ed., 1933, XXV, 674) report that the freezing point of whole-egg magma ranged from − 0.462° to − 0.470° C.

J. S. H.

Oak Forests of Pennsylvania.—According to A. C. MCINTYRE (Pennsylvania State College, School of Agric. and Exp. Sta., Bull. 283, 1933, 28 pages), "the oak forests of Pennsylvania are mainly of sprout origin, the product of cutting the virgin stands and the recutting of the second-growth. Many stands have been cut over three or four times, their regeneration being principally from sprouts." They contain 9 species of oak (white, chestnut, red, scarlet, black, pin, scrub, scrub chestnut, and swamp), of which the first 5 species predominate. These forests also contain at least 50 other species of trees. Under average conditions, the forests are growing at the rate of 0.6 cord per acre per annum. Growth of 1 cord per acre yearly occurs only on the better sites, such as moist fertile benches and coves. The forests are thrifty where fire has been kept out; probably less than 25 per cent. are normally stocked, but normality is approached with increasing age. They form an important economic resource of the state.

J. S. H.

Gelation of Frozen Egg Magma.—In the food industries, eggs are removed from the shell, mixed by churning, and cold stored hard frozen at a temperature of − 18° to − 21° C. When the frozen mass is thawed after storage for at least a few weeks, it usually is quite thick in consistency. ARTHUR W. THOMAS AND M. IRENE BAILEY (*Ind. Eng. Chem.*, Ind. Ed., 1933, XXV, 669–674) find that the degree of gelation of thawed whole-egg magma is governed by the mechanical treatment of the magma prior to freezing; the greater the disruption of the magma during churning, the lower is the resulting degree of gelation; colloid-milled specimens show practically no gelation. The degree of gelation becomes

greater the higher the per cent. of total solids or of ether extract (crude fat) in the magma. The degree of gelation is decreased by the addition of sodium chloride, dextrose, or sucrose to the magma; equimolecular quantities of glucose (dextrose) and sucrose produce the same effect; masses of sodium chloride (salt) and sucrose, which give rise to the same depression of the freezing point, apparently have the same effect on gelation. The degree of gelation is not governed by either the total phosphorus or the lipoid phosphorus content of the magma. The maximum gelation is attained during storage for 60 to 120 days.

J. S. H.

Vitamins of Tuna Meal.—ROGER W. TRUESDAIL AND LEE SHAHINIAN (*Ind. Eng. Chem.*, Ind. Ed., 1933, XXV, 661–662) have made biological assays of fresh, vacuum-dried meal prepared from the meat of the tuna fish (*Neothunnus macropterus*), chiefly the dark meat. The sample contained: Protein 62.09 per cent., ash 18.24 per cent., moisture 8.61 per cent., fat 8.04 per cent., crude fiber 0.50 per cent., free fatty acids 0.97 per cent. The meal was a good source of vitamin fat-soluble A, containing more than 14 units per gram, and an excellent source of vitamin fat-soluble D, containing more than 62 units per gram. These results suggest that the white meat of the tuna, which is canned and used as a food for man, may be a source of these vitamins in the human dietary.

J. S. H.

Toxic Gaseous Products of Combustion.—JOHN C. OLSEN, GEORGE E. FERGUSON, AND LEOPOLD SCHEFLAN (*Ind. Eng. Chem.*, Ind. Ed., 1933, XV, 599–603) have determined the gaseous products obtained when certain substances are decomposed by heat in the absence of oxygen, and when these substances are burned in the presence of an excess of air. The substances were cellulose (newspapers and wood), oils (gasoline), rubber insulation, wool, and silk. The gaseous products varied both qualitatively and quantitatively with the substance and the mode of heating, and included carbon monoxide, carbon dioxide, hydrogen, acetic acid, methane and other saturated hydrocarbons, unsaturated hydrocarbons, oxygen, nitrogen, hydrogen sulphide, sulphur dioxide, ammonia, and hydrocyanic acid. Silk and wool were sources of ammonia and hydrocyanic acid, and wool also yielded hydrogen sulphide and sulphur dioxide. Of the textiles, cotton and rayon gave rise to the least toxic gases, silk and especially wool to the most toxic gases. Inspiration of air containing more than 2 or 3 per cent. of carbon dioxide increases the respiratory rate. However, inspiration

of air containing acrid or ill-smelling gases decreases the respiratory rate and thus forces the individual to seek fresh air. These physiological effects thus aid in saving lives during fires by compelling people to leave the burning building.

J. S. H.

Selenium as an Insecticide.—C. B. GNADINGER (*Ind. Eng. Chem.*, Ind. Ed., 1933, XXV, 633–637) has discovered a new use for selenium. A solution of selenium in potassium ammonium sulphide, and containing a compound represented by the formula $(KNH_4S)_5$ Se, is highly toxic for the red spider. Thus a 30 per cent. solution of this compound was diluted 1 : 100 with 0.2 per cent. solution of high-grade soap, and then killed from 97 to 100 per cent. of the red spiders on infested plants. While this new selenide insecticide may be used on both flowers and plant food crops, it is still in an experimental stage. Thus its possible effect on plant foods with respect to their toxicity to the ultimate consumer must still be studied. The similar selenium product may be obtained, but it is not so toxic to insects, not so readily prepared, and less stable.

J. S. H.

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